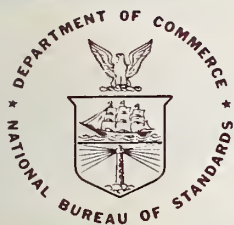


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Electrical Properties of Materials and Their Measurement at Low Temperatures

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Electrical Properties of Materials and Their Measurement at Low Temperatures

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ABSTRACT

A review is given of the electrical resistance of materials at cryogenic temperatures. Measurement techniques, the data base, and uses of the data are presented. The emphasis is on metals and alloys of technological importance; a topic which covers a large range of materials. Similarly, the treatment of theory and of measurement techniques is primarily for the user interested in the more practical aspects of the subject. In every instance, however, references are given which allow the reader to pursue the subject at any level.

Key words: alloys; conductivity; electrical property; metals; polymers; resistance; resistivity; review.

Chapter 1. LOW TEMPERATURE RESISTIVITY

The low temperature electrical resistivity of materials is one of the most useful of the physical properties. From it one can determine much about the chemical purity and mechanical state of a material. In more esoteric investigations, resistivity measurements provide detailed information on the electronic structure and other aspects of the basic physics of metals. In several instances, knowledge of the resistivity allows prediction of other properties, such as thermal conductivity, which are less convenient to measure. Resistivity is easily measured to reasonable accuracy for technological applications ($\sim 1\%$) and even very accurate measurements can be made with a modest investment in equipment. As one might expect, the literature on electrical resistivity is massive in quantity and, generally of high quality. Excellent tutorial treatments of all aspects of the subject are available.

In this monograph a condensed treatment of topics pertaining to resistance at cryogenic temperatures is presented: its measurement, the resistive mechanisms, and the data base. The emphasis is on metals and alloys of technological importance; a topic which covers an amazingly large range of materials. Similarly, the treatment of theory and of measurement techniques is for those interested in the more practical aspects of the subject. In every instance, however, references are given which allow the reader to pursue the subject at any level. Some words are appropriate here regarding what is not covered. There is no discussion of superconductors, semiconductors, or most insulators. Theory and experiment relating to single crystals or thin films are mentioned only when the information leads to a better understanding of the technologically important metals. These more basic topics are well described in the referenced texts.

No discussion of resistivity at low temperatures would be complete without special-mention of the book by Meaden [1], which is the most modern general treatment available, particularly concerning pure metallic elements. The data presented there and the extensive list of references covering the period to 1964 can save one many hours of labor with the original literature.

A word is in order here regarding handbook tabulations of resistivity data. The data presented in even the most recent editions of handbooks may be of ancient origin. These data may be very accurate, but many materials, particularly pure metals, are now produced by techniques resulting in significant increases in purity over those of earlier days. In many instances this change produces dramatic low temperature effects and is noticeable even in the room temperature resistivity. Some tabulations reference the sources of data, but most do not. In the latter cases it is best to view the information with skepticism.

Regarding the pure and commercially pure metals: there is no such thing as a low temperature resistivity for these metals. Changes in impurity and defect content, which are minor from an industrial standpoint may cause dramatic changes in the low temperature resistivity. For example, recent measurements of commercial copper satisfying the CDA102 specification (99.95% Cu + Ag) have given resistivity values at 4 K which range from 3 to 34 $n\Omega$ cm. This does not represent a failing of the manufacturer; in each instance the

copper is well within the specification. The message is clear: if the low temperature resistivity is an important parameter for the job at hand, it must be measured on the specific material to be used.

To indicate the large range of values covered by the electrical resistivity, consider figure 1.1, which presents typical resistivity data as a function of temperature for a number of metals and figure 1.2, which indicates the resistive behavior of a variety of copper products [2]. In table 1.1 ice point values for the resistivity of several common metals and alloys are listed. The measurements are reasonably recent except for some of those referenced to Hall which are "best values" derived from an extensive literature survey. In each case the materials are very well characterized in the references. A value of the residual resistivity ratio RRR^1 is also given in the table.

Most of the figures presented here are prepared using data from the literature. Often it was necessary to extract those data from small graphs, so that the exact numerical values shown here may not be very accurate. These curves are intended to indicate general behavior only; for accurate data, the referenced sources should be consulted.

¹ RRR - Residual Resistivity Ratio = $\rho(273\text{ K})/\rho(4\text{ K})$. In metals of commercial purity or better, the numerator depends essentially only on the thermal vibrations of the lattice and not on the impurities. The denominator depends only on the impurities and defects for most metals, and thus the ratio is a sensitive indicator of purity; in fact, it is capable of detecting impurity levels far below those which can be seen by most analytical techniques. To first order, the ratio is independent of shape factor, i.e., it is equal to the ratio of the resistances. In highly alloyed metals, the ratio is not as meaningful and is useful only in comparing samples of nominally similar composition.

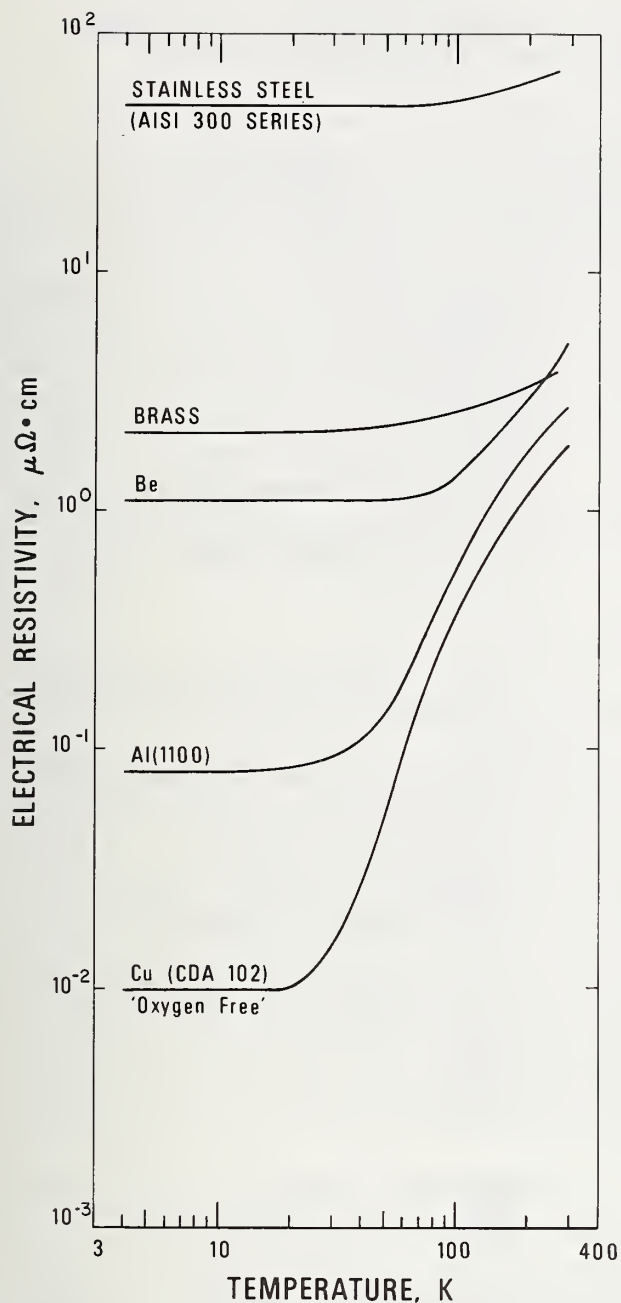


Figure 1.1. Resistivity of several common metals as a function of temperature.

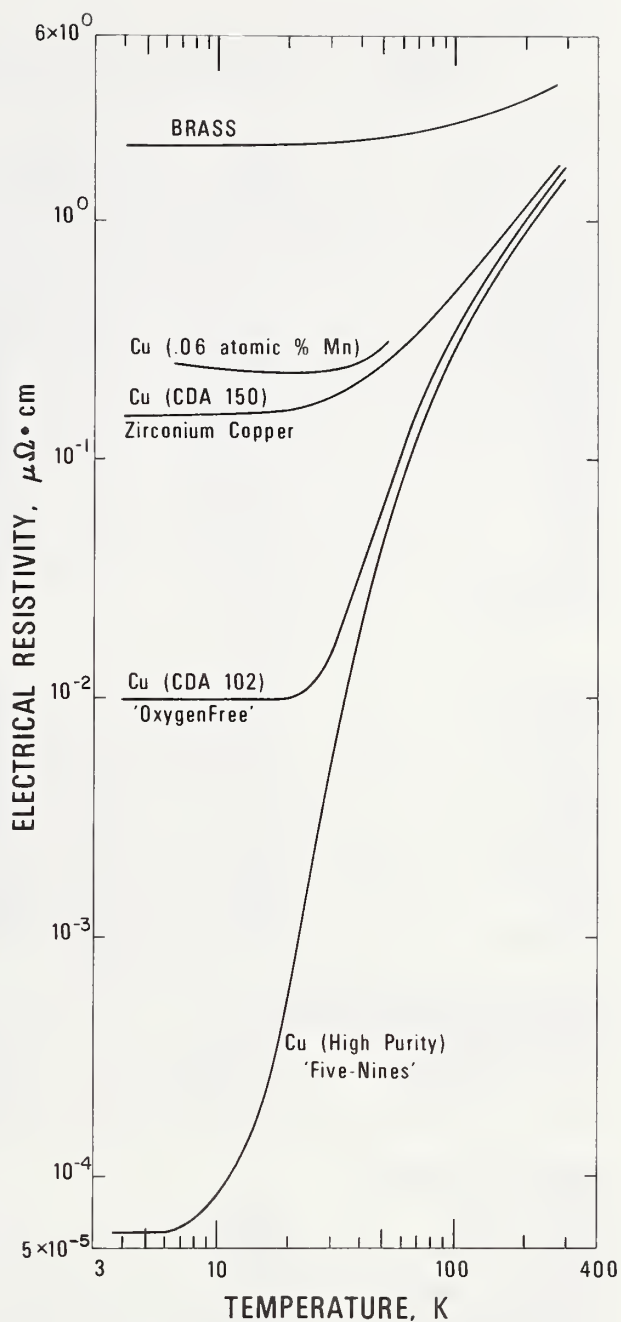


Figure 1.2. Resistive behavior of a number of "pure" coppers and copper alloys.

Table 1.1. Resistivity of selected metals and alloys at the ice point

Material	ρ ($\mu\Omega\text{cm}$)	Reported RRR $\equiv \rho(273\text{ K})/\rho(4\text{ K})$	Reference
<u>Pure metals</u>			
Aluminum	2.428	40,000	Fickett [3]
Beryllium ^a	2.70	75	Reich [4]
Cobalt	5.24	60	Hall [5]
Copper	1.553	12,000	Fickett [6]
Chromium	12.155	213	Hall [7]
Gold	2.058 ^c	300	Hust [8]
Indium	8.00	13,000	Hall [5]
Iron	9.07 ^c	23	Hust and Giarratano [9]
Lead	19.2	15,000 ^d	Hall [5]
Magnesium ^a	4.12	285	Hedgcock and Muto [10]
Manganese ^b	α 143.5	α 16	Hall [7]
	β 91.0		
	γ 22.7		
Molybdenum	5.0	22	Hall [5]
Nickel	6.23 ^c	270	Laubitz, Matsumura, and Kelly [11]
Niobium	13.96	1500 ^{d,e}	Hall [5]
Platinum	9.60	755	Ibid.
Sodium	4.337	\sim 500	Cook, Van der Meer and Laubitz [12]
Silver	1.48	2000	Hall [5]
Titanium ^a	39.4	33	Hall [5]
Tungsten	4.94	80	Hust and Giarratano [13]
Tin ^a	10.1	63,000 ^f	Hall [5]
Zinc ^a	5.45	1400	Babic, Ocko, and Rizzuto [14]
<u>Commercially pure metals</u>			
Aluminum 1100	2.67	32	Clark, Childs, and Wallace [15]
Copper CDA 102	1.56	97	Ibid.
CDA 150	1.73	11	Ibid.
Nickel TD	6.73	39	Ibid.
<u>Commercial alloys</u>			
Bronze, 90%	3.90	1.8	Ibid.
Naval Brass	6.32	1.6	Ibid.
CuNi30	38.4	1.05	Ibid.
<u>Stainless Steels</u>			
NBS-SRM	78.6	1.32	Hust and Giarratano [16]
AISI 304L	70.4	1.42	Clark, et al. [15]
AISI 316	75.0	1.39	Ibid.
AISI 321	73.9	1.38	Ibid.
AISI 410	55.9	1.46	Ibid.
Invar 36	79.5	1.58	Ibid.
Ti-6Al-4V	167.5	--	Ibid.

a. Anisotropic resistivity observed in single crystals. Data are for polycrystalline specimens.

b. Allotropic metal.

c. Interpolated value.

d. Superconducting above 4.2 K. Magnetic field applied.

e. 4 K data from Keil, Merbold and Diehl [17]

f. 4 K data from Boato, Bugo and Rizzuto [18]

Chapter 2. EXPERIMENTAL TECHNIQUES AND CONSIDERATIONS

Resistivity is one of the easiest of all physical properties to measure. The basic techniques and apparatus are described in detail by Meaden [1] and by Gerritsen [19] as well as in many electrical measurements texts such as those by Stout [20], Gregory [21] and Wolf [22]. The Kelvin bridge method and the potentiometer method are two of the most useful classical measurement techniques. They both offer better than 1% accuracy in micro-ohm level measurements. Most of the textbook methods are quite time consuming, and the approaches actually used in most laboratories are somewhat less sophisticated, since time is often of the essence and high precision is not usually required. Several of these easier techniques are described here; the more esoteric ones are left to the authors referenced above.

The equation from which the resistivity, ρ , is most often calculated is

$$\rho = RA/\ell = VA/I\ell \quad (2.1)$$

where R is the resistance of the specimen, V the voltage measured, I the current, A the cross sectional area of the specimen and ℓ the length between the voltage probes. With reasonable care, both A and ℓ can be determined to 0.5% and, of course, to greater precision in a carefully designed experiment. The usual technique of determining an average wire diameter for the calculation of A will lead to incorrect results if there are significant variations in diameter along the specimen. Most experiments are designed such that the voltages to be measured are on the order of microvolts or greater. This leads to practical specimen sizes and current levels, as well as giving a voltage measurable with good accuracy by relatively inexpensive equipment. Furthermore, equipment such as this is easily adapted to the many modern computer control methods for automated operation.

2.1 Direct current measurements

A direct current (dc) system, which has been used successfully for routine measurements, is shown in figure 2.1. The current source can be anything from an automobile battery to a precision current calibrator. It should be stable over the time required for a measurement. The standard resistor is chosen primarily to have a sufficiently low resistance that it will not suffer any significant heating at the highest currents. Allowable power dissipation limits are stated by the manufacturers -- they are lower than one might expect, so it is well to check them. Reversal of the current is essential to eliminate thermoelectric voltages, a complication to be discussed shortly. The use of a commercial nanovoltmeter with its output read by a relatively inexpensive digital voltmeter provides good precision ($\sim 1\%$) with minimum cost and allows for greater flexibility in an environment where instruments must often be shared among several experiments. The use of a four-probe system for the leads (i.e., separate sets for current and voltage) is the best approach to low level dc resistance measurement; two-lead systems introduce too many possible sources of error.

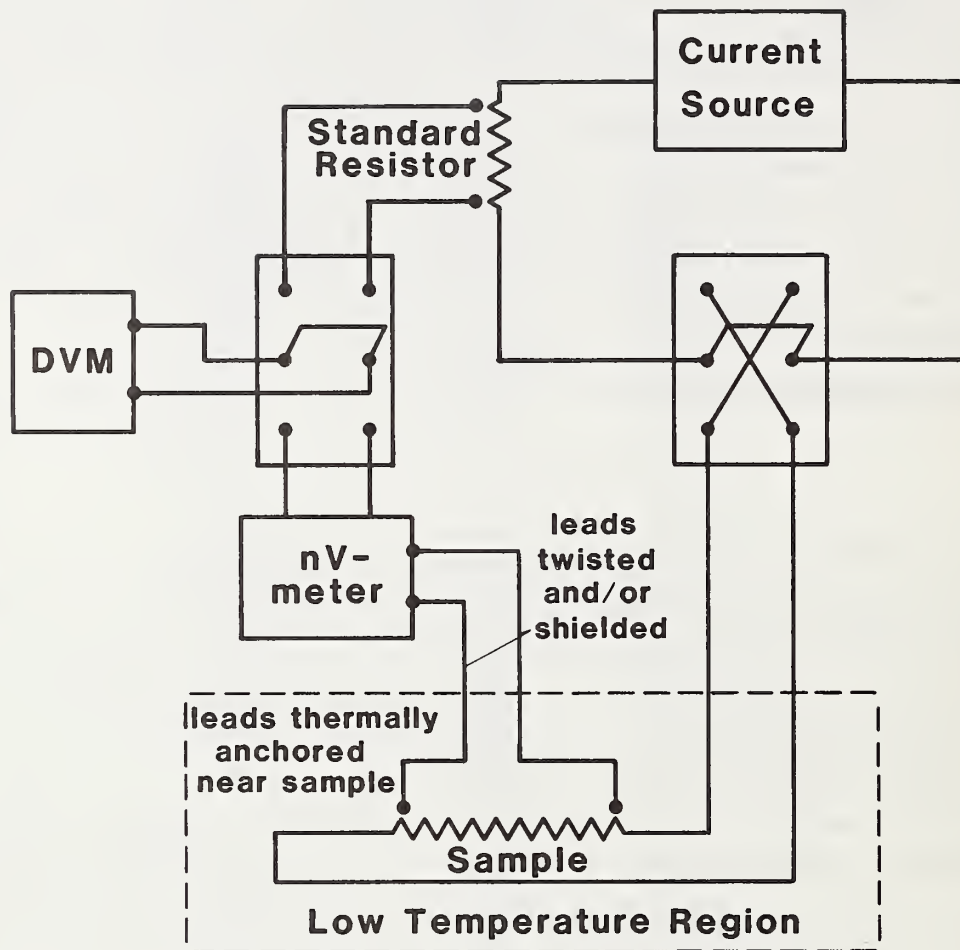


Figure 2.1. Block diagram of a system for low temperature resistivity measurements.

2.2 Alternating current measurements

At first glance, alternating current (ac) techniques, particularly those involving modern lock-in amplifiers seem to offer many advantages in low temperature resistance measurements, particularly in the elimination of thermal voltages. In practice, however, rather heroic techniques are necessary to make accurate measurement of resistances smaller than $1\ \Omega$ [23]. On the other hand several very nice ac bridge circuits have been developed for relatively high-resistance thermometry applications at low temperatures [24,25]. The only source of detailed information on lock-in measurement techniques applicable to low temperature resistivity measurements appears to be in the manufacturers' literature. Shielding and grounding, along with the correct use of transformers, are the major problems in such an application and are discussed in detail by Morrison [26].

2.3 Eddy current method

An ac technique which has proven very useful in relative resistivity determinations is the eddy current decay method. The basis for the method is described by Bean, DeBlois, and Nesbitt [27] and a description of a working system is given by Clark, Deason, Hust, and Powell [28]. A schematic of the apparatus is shown in figure 2.2. While not particularly accurate (1 to 5%) as a resistivity measurement, the system is extremely fast. Furthermore, it is not necessary to attach leads to the specimen and resistivity ratios of specimens of odd shapes and sizes can be measured easily. The system is relatively expensive and parts of it must be homemade. For experiments requiring repeated low temperature measurement on the same specimen, such as annealing recovery curves or impurity segregation experiments, it is a valuable tool. An adaptation of this technique to measurements of the anisotropic resistivity observed in some metals (see section 3.1) is described by Lawson [29].

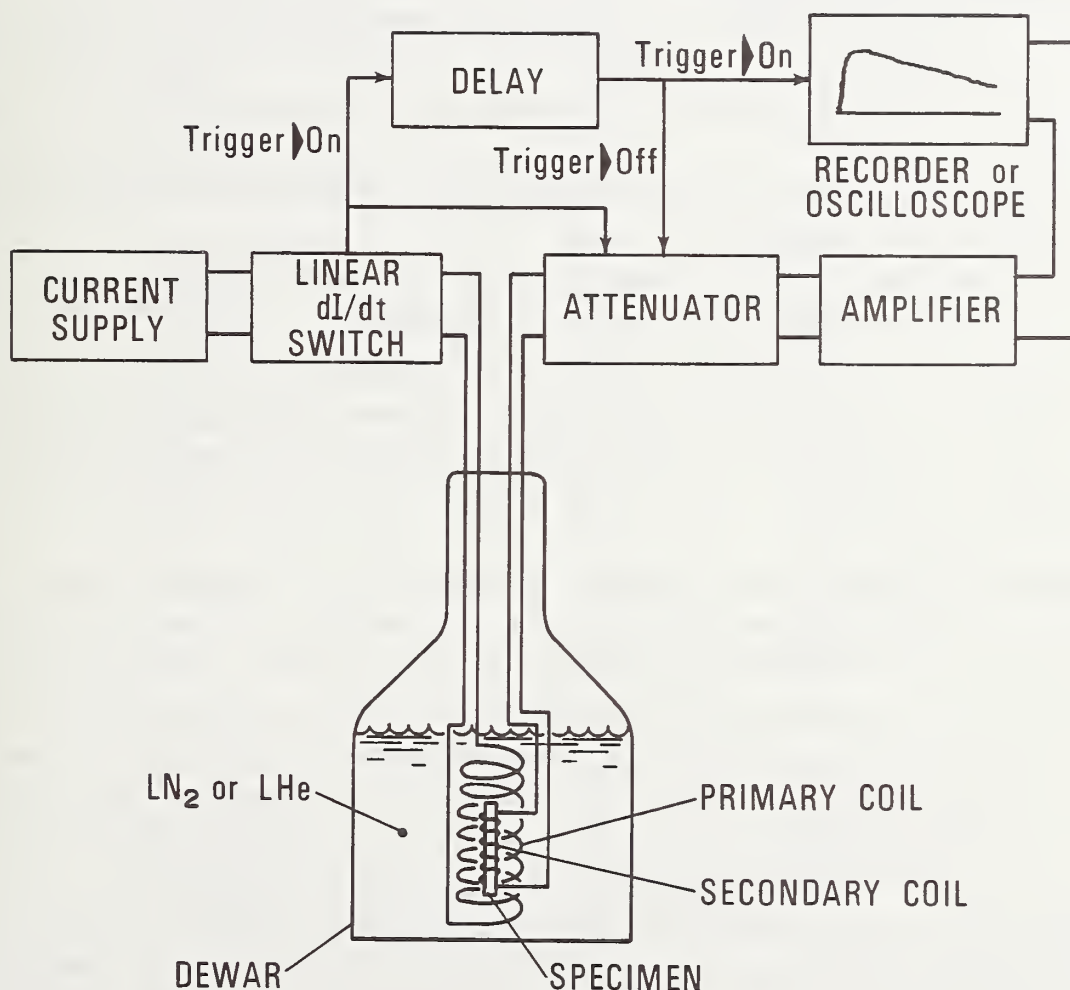


Figure 2.2. Apparatus for the eddy current decay technique. A recorder is used to display long time-constant traces (large specimens of very pure metals) and an oscilloscope for shorter time constants.

2.4 Low level measurements

The relatively easy methods just described do not always suffice. The most frequent failing occurs when voltages well below the microvolt level must be measured. In fact, nanovolt signals are commonly encountered in physics experiments on pure metals. In spite of the availability of commercial nanovoltmeters and potentiometers on the market, measurements at this level are very difficult and measurements with 1% accuracy require very specialized apparatus. A nanovolt detection system using commercial components is described by Clark and Fickett [30]. An extensive discussion of techniques using SQUID (Superconducting Quantum Interference Devices) detectors is given by Gifford, Webb, and Wheatley [31]. Other devices, which convert the low level dc voltage to ac in the cryostat and subsequently amplify the resulting signal, have been described in the literature. Magnetic amplifiers [32], Hall effect amplifiers [33], superconducting modulators [34], and relay modulators [35] have all been used in this manner.

2.5 Additional considerations

Low temperature measurements introduce other special problems of a technical nature that must be considered:

- a. The temperature of the specimen must be accurately measured and precisely controlled.
- b. At low temperatures, joining techniques for current and voltage leads are more critical than at room temperature.
- c. Voltage leads traverse a large temperature gradient, leading to spurious thermal voltages and creating unwanted paths for heat conduction.
- d. Uneven thermal contraction of parts of the apparatus can stress the sample.

In addition to these, there are more basic phenomena which can create havoc for the unwary, such as size effects and large resistance changes due to magnetic fields or phase transformations. These are covered in later chapters. Here we discuss only the four topics listed above.

Temperature control. When resistivity measurements as a function of temperature are necessary, the experimental setup becomes much more complex. In some instances, one can take an easy way out by immersing the specimen in various constant temperature baths. The most common baths are liquified gases and slushes (solid-liquid mixtures) of organic fluids, usually prepared by mixing with liquid nitrogen [36]. Some of the temperatures attainable by this method are listed in table 2.1. The temperatures of the liquid gas baths are dependent on pressure and, thus, on elevation; for example, liquid helium boils at 4.0 K at Boulder, Colorado (elevation 1610 m) vs. 4.2 K at sea level. It should not need emphasis that liquid hydrogen and liquid oxygen should be used only by those familiar with their unique capabilities for total destruction of the laboratory. Some caution is also necessary with many of the organics. It is common practice to mix crushed dry ice with either acetone or alcohol to make a liquid bath at dry ice temperature. Any cryogenic bath should be contained in an insulated container for stability and longevity. Vacuum pumping of cryogenic liquids, combined with some form of pressure control, such as

a manostat system, allows attainment of ~ 1 K with helium, 14 K with hydrogen, 25 K with neon and 64 K with nitrogen, but the resulting system complexity seldom justifies such an approach except for the case of helium, where only more complex options (e.g., dilution refrigerators) are available. The entire range of specialized techniques for producing and measuring temperatures below 1 K is described by Betts [37] and not discussed here. In all other cases the heater temperature control techniques described below are more practical.

Table 2.1. Liquified gas and slush bath temperatures.

Substance	Temperature (K) ^a	Bath Type
Ice water	273.15	Slush
Isobutane	262.9	Liquid B.P.
Carbon tetrachloride	250	Slush
Propane	230.8	Liquid B.P.
m-xylene	226	Slush
Trichloroethylene	200	Slush
Carbon dioxide	194.6	Solid
Methanol	175	Slush
n-pentane	142	Slush
Iso-pentane	113	Slush
Methane	111.7	Liquid B.P.
Oxygen	90.1	Liquid B.P.
Nitrogen	77.3	Liquid B.P.
Neon	27.2	Liquid B.P.
Hydrogen	20.4	Liquid B.P.
Helium (He ⁴)	4.2	Liquid B.P.
Helium (He ³)	3.2	Liquid B.P.

^aAll temperatures given at 0.1 MPa (1 atm).

Continuous temperature control may be performed by a variety of techniques. White [38] discusses several methods in general outline and includes references to the literature. The technique of electrically heating a copper block in good thermal contact with the specimen, but partially isolated from the coolant bath by a properly chosen heat leak, is the usual choice. The electronics for temperature control are available commercially

or can be built rather easily. The electrical concepts are discussed by Forgan [39]. A precision at low temperature of ~ 50 mK is easily obtained; 1 mK requires some care. Systems have been described in the literature that offer control to 50 μ K [40], or even 1 μ K [41]. A much less sophisticated technique is sometimes adequate in which the specimen and a heat-sink block containing a thermometer are immersed in liquid helium for a 4 K measurement and then removed to the space above the liquid and allowed to drift upward in temperature. With the use of a stable x-y recorder, this technique is a good method for looking for "glitches" in the resistivity caused by phase transformations, etc. The temperature profiles of a particular dewar configuration have been measured by Crooks [42].

Bonding of specimens. In most instances, a good thermal bond between the specimen and the heat sink block is important because thermometers are usually attached to the heat sink rather than to the specimen. It is nearly always desirable that the bonding agent be an electrical insulator. The most common materials are an electrical varnish and various greases. Thermal conductivity values for these materials have been measured [43,44]. When constructing a new apparatus, the specimen-heat sink temperature difference should be checked, possibly with a differential thermocouple arrangement. With reasonable care, the thermal contact should be adequate for moderately precise work.

Temperature measurement. The measurement of low temperatures is discussed in many texts, two of the most useful are those by Meaden [1] and White [38]. Rubin [45] has published an extensive review. Low temperature tables are now available for many standardized thermocouple types [46]. Table 2.2 lists some of the more common thermometers used at 4 K and above and their properties. An excellent discussion of these transducers and several others such as gas thermometers, is given by Sparks [48]. The problems of bonding, mentioned above, and of thermal anchoring, are very important.

Lead attachment. The method of attaching the potential leads and, to a lesser degree, the current leads to the resistivity specimen requires some consideration. Pressure contact arrangements are often adequate for measurements made in a liquid bath. All kinds of steel knife edges, brass screws with sharp points and fine, bare copper wires, have been used. Spring loading of the contacts at room temperature seems to work well--almost any spring material will do. Attention must be paid to the relative thermal expansion of various parts of the sample holder. Pressure contact systems have the advantage of precise location of the probes and minimum disruption of the specimen. It has been the author's experience that pressure contacts never work well in a high magnetic field. Excessive noise always seems to occur on the voltage signal. When measurements are to be made over a temperature range or in a magnetic field, soldering, spot welding, or welding appear to be the only reasonable techniques. Solders are available with melting points from below 373 K (BiPbSn) to about 473 K (PbSn). They are nearly all superconducting, and some have critical temperatures in excess of 7 K and critical fields near 1 T [49]. Normally this superconductivity presents no problem, but it can cause trouble in specific experiments. Soldering of potential leads generally gives a large contact area and decreases the precision with which the probe separation can be measured.

A complex, but successful technique for increasing this precision involves: coating the specimen with varnish, curing, drilling a 0.2 mm diameter hole to the metal surface, inserting a 0.12 mm flux coated ball of low melting point solder (available commercially), heating to melt the solder, and inserting a pre-tinned potential lead. Spot welding can be used for nearly any combination of metals, but it is easiest for higher resistivity materials. Often an intermediate metal such as nickel must be employed. Some arrangements, such as joining a small diameter copper wire to one of large diameter, will tax the skill and patience of the most accomplished welder. The major problem with spot welding leads is the possibility of major damage to the specimen by mechanical deformation or arc burn. Welding, usually used for joining fine wires, is a reliable technique if a small oxy-hydrogen torch is available.

Table 2.2. Thermometers for the measurement of low temperatures

Type	Temperature Range (K)	Comments
<hr/>		
Liquid in glass		
Toluene	180-320	
Pentane	70-300	An impure pentane.
Thermocouple		
Type E	20-300	Useful also above room temperature.
Type KP or EP vs. Au.07at.%Fe	4- 20	Can be used to room temperature ^a
Metal resistor		
Platinum	10-300	Can be used to 1200 K - usual application is above 50 K.
Copper	20-300	Not commercially available.
Indium	4-300	Not commercially available.
Semiconductor		
Germanium	4-100	Very sensitive to magnetic fields.
Thermistor	4-300	Very sensitive to magnetic fields.
Carbon resistor	4-100	Inexpensive, less field sensitive than the semiconductors.
<hr/>		

- a. AuFe is not a standardized thermocouple type but is available commercially. Tables are given by Sparks and Powell [47].

Thermal considerations for lead wires. The conduction of heat to the specimen by the leads can occasionally be troublesome. In such cases leads of high thermal resistance alloys, such as constantan, Evanohm, or manganin are sometimes used. The alloys have similarly high electrical resistances. Theoretical aspects of the problem and some practical calculations are presented by Mercouroff [50]. A more common solution is to use copper wire, but to anchor a reasonable length of the lead to a heat sink block which approximately tracks the specimen in temperature [51]. This technique has the added advantage of minimizing spurious thermal emf's. These thermoelectric voltages, generated in the presence of thermal gradients, arise from contacts between dissimilar metals and from inhomogeneities in the lead material. Spurious voltages in a well-designed experiment should be stable at the submicrovolt level over short time periods. All dc potential measurements should be an average of two readings taken before and after reversing the sample current.

Thermal contraction. Relative thermal contraction may cause serious problems in electrical measurements at low temperatures due to the wide range of behavior exhibited for various classes of common materials [2]. Clearly, a pure metal rigidly attached to a plastic substrate will be strongly compressed on cooling. The usual result of such an arrangement is that the metal tends to buckle. The obvious solution is to allow some motion of the specimen in the holder. Another is to make the entire holder from the same type of materials as the specimen, e.g., a copper holder for pure metals, and rely on thin varnish coatings and polymer films for electrical insulation. A final possibility is that of matching the expansion coefficient of the holder material to that of the specimen. This can be accomplished by the use of filled epoxies [52] or, possibly, graphite-epoxy composites of suitable composition [53].

Chapter 3. PURE METAL RESISTIVITY

Many separate mechanisms influence the electrical resistivity of pure metals and alloys. Some of these effects become particularly important at low temperatures. In the following sections, brief descriptions of the various mechanisms that are operative in producing resistance at low temperatures are presented. Clearly, not all of them are important in every metal or configuration. Solid state physics texts contain the theoretical details; the following sections continue in a pragmatic vein.

3.1 Intrinsic resistivity

The intrinsic resistivity is that of a pure, perfect metal and arises from the scattering of electrons by lattice vibrations (phonons). No such perfect metal exists, of course, but at room temperature the intrinsic component is usually the dominant contributor to the resistivity of pure metals. It is also the most temperature dependent of the mechanisms.

Conceptually, experimental determination of the intrinsic resistivity is quite easy. One measures ρ versus T and obtains a curve like that for pure copper in figure 2.1. The assumptions are made that the resistivity observed at the low temperature end of the curve is due entirely to other mechanisms and is not temperature dependent. This "residual" resistivity is then subtracted from all measured values and a new curve is created representing the intrinsic resistivity, ρ_i , which now is a true property of the metal. Often, the curve can be fit to the Bloch-Gruneisen form

$$\rho_i = \frac{K}{\theta} \left(\frac{T}{\theta}\right)^5 \int_0^{\frac{\theta}{T}} \frac{e^z z^5 dz}{(e^z - 1)^2} \quad (3.1)$$

by judicious choice of the characteristic temperature, θ . K is a constant. Meaden [1] explains a variety of methods for determining θ and Rogers and Powell [54] give an extensive tabulation of values for the integral. Most common metals have θ values between 300 and 400 K (copper \approx 330 K, aluminum \approx 395 K) although some are well outside this range (beryllium \approx 1200, sodium \approx 200). At either end of the temperature range the equation reduces to a more simple temperature dependence:

$$\rho_i \propto T \text{ for } T \gtrsim \theta/2, \quad (3.2)$$

and

$$\rho_i \propto T^5 \text{ for } T \lesssim \theta/10. \quad (3.3)$$

The linear behavior is almost always observed near room temperature, as it should be, but often not at very high temperatures. The temperature coefficient of resistance, α , defined as:

$$\alpha = (R_{T_2} - R_{T_1}) / R_{T_1} (T_2 - T_1) \quad (3.4)$$

is tabulated in the Metals Reference Book [55] for metallic elements and for some alloys for $T_1 = 273$ K and $T_2 = 373$ K. Common pure metals tend to have values from 4 to $6 \times 10^{-3} \text{ K}^{-1}$ (copper and aluminum: $\alpha \approx 4.2 \times 10^{-3} \text{ K}^{-1}$), and alloys generally $< 2 \times 10^{-3} \text{ K}^{-1}$ (AISI 304 stainless steel: $\alpha \approx 1.2 \times 10^{-3} \text{ K}^{-1}$).

The low temperature behavior expressed by eq (3.3) is not often observed. The experiment involves measuring the small difference between two nearly equal numbers, usually under very difficult experimental conditions. The author has tabulated the various temperature dependences reported for the resistivity of aluminum below $\Theta/10$ [3]. They range from T^5 to T^2 . Similarly copper has been reported to have a low temperature behavior from nearly T^6 [56] to T^5 [6] depending on purity. Ferromagnetic metals show even more complex behavior. In fact, it appears that there may well be no such thing as a temperature dependence for a real metal.

The conclusions that can be drawn from the above about the intrinsic resistivity are: (a) most metals show a linear dependence of ρ on T near room temperature, which is not greatly affected by low levels of impurities; (b) departures from linearity often occur at higher temperatures; (c) below about 20 K there is no dependable expression for the intrinsic resistivity of most metals; (d) above about 20 K, eq (3.1) usually provides a good estimate of ρ_i up to room temperature for well behaved metals. One shouldn't be too concerned about (c), since the resistivity of most useful metals is residual at low temperatures and the temperature dependent part represents only a very small portion of the resistivity. For example, at 4 K the intrinsic resistivity of copper is $\sim 3.5 \times 10^{-7} \mu\Omega \text{ cm}$ ($\text{RRR} = 4.4 \times 10^6$) and that of aluminum is $\sim 6 \times 10^{-7} \mu\Omega \text{ cm}$ ($\text{RRR} = 4.0 \times 10^6$). These values are far above the best resistivity ratios measured experimentally (see table 1.1).

Anisotropic metals. Metals with noncubic crystal structure show an orientation dependent resistivity (anisotropy). Several are indicated in table 1.1. With the exception of tin, they are all hexagonal metals. The ratio between the resistivity parallel to the c axis and that normal to it, as determined from single crystal measurements, is given in table 3.1. Meaden [1] lists many more in his Table III. He also discusses the manner in which one should combine the two resistivity values in order to arrive at an average resistivity, $\bar{\rho}$, for a polycrystalline material. For nearly all real metals, a reasonably accurate equation is:

$$\bar{\rho} = (2\rho_{\perp} + \rho_{\parallel})/3 \quad (3.5)$$

which is slightly different from the more often quoted formula used by Hall [5]. A comprehensive theoretical treatment covering very large anisotropies and resulting in more accurate (and significantly more complex) equations is presented by Hashin and Shtrikman [58a].

Anisotropy effects must be expected when rolled or drawn product forms are made from the noncubic metals and alloys. Because of preferential elongation of grains with certain

orientations, the material resistivity may differ significantly from what one might expect from the above discussion.

It is difficult to make any statement about the relative temperature dependence of the directional resistivities because of the limited data. Nevertheless, it seems that for most metals, no dramatic change in the ratio $\rho_{||}/\rho_{\perp}$ occurs on cooling to cryogenic temperatures. This was observed to be the case by the author in measurements on the highly anisotropic metal, mercury ($\rho_{||}/\rho_{\perp} = 0.76$) [59]. On the other hand the data on zinc by Aleksandrov and d'Yakov [58] show a variation of $\sim 20\%$ in the ratio, but it apparently occurs in a random manner.

Table 3.1. Resistivity values of anisotropic metals

Metal	Temperature (K)	$\rho_{ }/\rho_{\perp}$	Reference
Be	273	1.14	Ha11 [5]
Mg	273	0.83	Ibid.
	78	0.85	Ibid.
Ti	273	1.06	Wasilewski [57]
	77	0.90	Ibid.
Sn	273	1.45	Aleksandrov and D'Yakov [58]
	77	1.58	Ibid.
	4.2	1.35	Ibid.
Zn	273	1.04	Ha11 [7]
	77	1.14	Aleksandrov and D'Yakov [58]
	4.2	0.92	Ibid.

Crystallographic transformations. A number of pure metals, and nearly all alloys, possess more than one stable crystallographic phase. The change from one phase to another may be caused by a variety of mechanisms such as temperature, pressure, tensile strain, or certain impurities. The subject is one of a great deal of interest in metallurgy and materials science. There are many excellent general texts, such as the one by Christian [60]. Most such transitions occur above room temperature, but the higher temperature phases can often be obtained at room temperature and below by proper (or accidental) quenching techniques. Here we present a brief introduction to the resistive behavior.

The different phases of a metal may have vastly different resistivity values as indicated by the data for manganese in table 1.1, which show nearly a factor of seven

variation in the ice point resistivity. The α phase of manganese is the normal one at room temperature; the others are higher temperature phases. Transformations seldom proceed to completion, and as a result, the specimen becomes a mixture of the two phases - a situation that can lead to bizarre temperature dependences for the resistivity since the mix of the phases is usually temperature dependent itself. To further complicate the problem the process, although usually reversible, exhibits a large temperature hysteresis. The good news is that very few pure metals have crystallographic transformations below room temperature [61]. Lithium transforms to hexagonal (hcp) on cooling to ~ 77 K, Na at ~ 36 K. Face centered cubic (fcc) phases can be induced in these metals by deformation. Tin is tetragonal above 286 K and may have a diamond structure below that; cerium goes from fcc to hcp to fcc in a complex series of transformations spanning the range from ~ 265 K to 90 K. Gerritsen [19] tabulates the resistivity changes that occur upon transformation for these elements (and many others that undergo phase changes above room temperature). His data show that tin changes to a semiconductor; and cerium shows a decrease in resistivity as the temperature is lowered through the transition temperature. No change is shown for lithium or sodium, but a later measurement on lithium by Dugdale and Guban [62] shows a large cusp in the resistivity versus temperature curve at about 70 K. The cusp is seen on lowering temperature, but is nowhere near as obvious in the increasing temperature measurement.

Magnetic transformations. Low temperature magnetic transformations, usually from paramagnetism to antiferromagnetism to ferromagnetism as the temperature is lowered, occur primarily in the rare earth elements. These transitions result in an odd resistivity behavior with temperature [63]. Of the more common metals, α -manganese shows the first of these transitions over the range 70-90 K [64], as does chromium near room temperature [65]. Figures 3.1 and 3.2, from the references, show the observed resistivity behavior. Similar transformations are seen in many of the ferrous alloys. Pure soft ferromagnetic materials, such as iron, show a strong dependence of the low temperature resistivity on measuring current at very low current values. An excellent example is provided by the work of Takaki and Igaki [66], which shows a variation of RRR from 500 to 170 as the measuring current density is increased to 6 A mm^{-2} . One should add that applying a small longitudinal field of 40 kA m^{-1} (500 Oe) to the specimen increased the RRR to 2500. This effect most likely results from the removal of domain walls, which scatter the conduction electrons. The theory and some experimental work on electron scattering interactions in magnetic materials, such as electron-electron and electron-magnon scattering are reviewed by Volkenshtein, Dyakina, and Startsev [67].

3.2 The effect of impurities

The materials considered here are those in which the impurity metals are in solid solution. In general, these alloys contain less than a few atomic percent of impurities. These may be ones that occur naturally in the metal or that have been introduced for experimental purposes. The effect of low levels of impurities on the resistivity of commercially pure conductors is of primary importance, particularly at low temperatures,

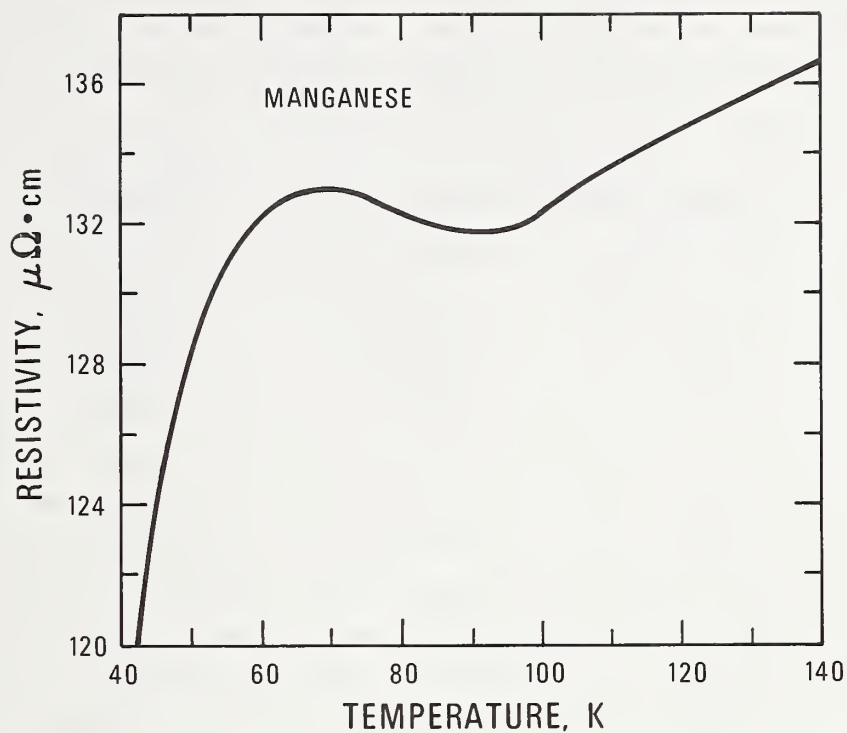


Fig. 3.1 Resistive behavior of α -manganese. The metal is antiferromagnetic below ~ 100 K [64].

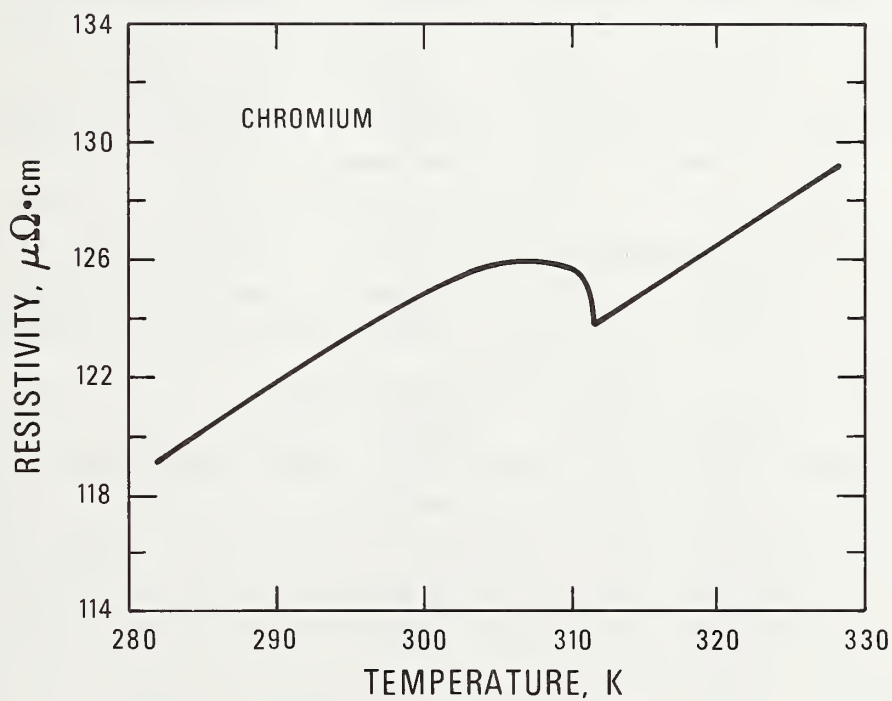


Fig. 3.2 Resistive behavior of annealed chromium. The metal is antiferromagnetic below ~ 310 K [65].

where the impurity resistivity often represents the major contribution to the total. Most of the experimental work on the resistive contribution of various impurities was done prior to about 1970. The experiments are not as easy to carry out as one might expect. The production and proper chemical analysis of dilute alloy specimens is difficult, and particularly in the case of analysis, few laboratories have adequate facilities. Analysis below about 0.1 atomic percent is subject to large (20 to 50%) errors for many elements. The purity of the solvent metal is often known imprecisely. The analysis supplied with the metal is often a general analysis for that type of metal and not specific to the piece supplied. Furthermore, precipitation, compound formation, agglomeration and migration of the solute to grain boundaries can occur even at very low concentrations. These situations are not detected by conventional analysis and always result in a resistivity contribution that is below that for the true solid solution. As an example, the resistivity of iron in copper at 4 K has been observed to decrease from $1.81 \mu\Omega \text{ cm/at.ppm}$ (observed up to 100 ppm) to $1.48 \mu\Omega \text{ cm/at.ppm}$ for alloys containing 750 and 690 at.ppm Fe [68]. Magnetic measurements on the higher content alloys suggest the precipitation of γ -iron.

In the following subsections, the effect of various impurities on the low temperature resistivity of pure metals and its temperature variation are discussed. The topic is one that has been reviewed often and well and this treatment relies to a large extent on those reviews.

Impurity resistivity at fixed temperature. The contribution of impurity elements to the resistivity of pure metals has been studied extensively. Most of the available data are at room temperature, although a significant amount of low temperature data exists. Table 3.2 shows aluminum data collected by the author [3] and copper data from the extensive compilation by Welles [69]. Blatt [70] presents a table covering some 40 metals as solutes in copper, silver, gold, aluminum, magnesium, lead, titanium, iron, nickel, palladium, and platinum. No indication is given of the temperature of measurement or the data sources. A table of earlier data is also presented by Gerritsen [19]. The data in the literature in general are not as convincing as one would like. In nearly every case, measurements by different experimenters result in widely different numbers, often varying by 20 to 30% for the same alloy. Thus, there is still a need for a comprehensive series of measurements on alloys that are very well characterized both chemically and metallurgically. Unfortunately, such a task could take a lifetime.

Some general statements can be made: Impurity elements in solution always cause the resistivity to increase. The increase appears to be always linear with concentration as long as the impurity remains in solution. The contributions of solute elements are additive, allowing calculation of low temperature resistivity from a good chemical analysis. In nearly all instances, the resistive contribution of an impurity measured at room temperature is within about 5% of the value found at 4 K. The low temperature value is usually higher.

In some instances, it is possible to increase the amount of impurity in solution far above the room temperature solubility by very rapid quenching of the alloy. The technique is described by Ocko, Babic, Krsmik, Girt, and Leontic [71] and in earlier work by the

Table 3.2. Resistive contributions of impurities to copper and aluminum

Impurity element	$\Delta\rho(\mu\Omega\text{cm/at.}\%)$	
	Copper	Aluminum
Al	0.95	--
Ag	0.1	1.0
As	6.7	0.5
Au	0.55	--
Be	0.65	0.4
Bi	5.7	1.3
Ca	1.0	0.3
Cd	0.3	0.57
Co	6.9	3.6
Cr	4.0	8.4
Cu	--	0.83
Fe	9.3	5.4
Ga	1.4	0.24
Ge	3.7	0.79
Hg	1.0	--
In	1.1	--
Ir	6.1	--
Li	--	0.86
Mg	0.8	0.46
Mn	2.9	6.9
Mo	--	7.5
Na	--	2
Ni	1.1	1.6
Pb	3.3	1.2
Pd	0.95	--
Pt	2.0	--
Po	8.5	--
Re	4.4	--
Sb	5.5	0.9
Sc	--	5
Se	10.0	--
Si	3.1	0.72
Sn	3.1	0.9
Te	8	--
Th	1.8	--
Ti	16	5.5
V	9.7	6.8
W	--	7.3
Zn	0.3	0.23
Zr	1.3	5.8

same group. Their studies indicate that the value of the specific impurity contribution to the resistivity is maintained to quite high percentages of solute.

The effect of temperature. Near room temperature the dilute alloys maintain the linear dependence of resistivity on temperature observed for the pure solvent. However, the slope is seriously affected by the impurity. In particular, $d\rho/dT$ is found to decrease with increasing content of magnetic elements and to increase otherwise. This behavior is discussed by Gerritsen [19]. He presents a graph for copper alloys showing a linear dependence of the temperature coefficient of resistivity on the room temperature electrical conductivity.

At low temperatures, the resistivity of annealed alloys is nearly always dominated by the impurity content, and usually this residual resistivity is effectively a constant below 4 K. It is generally assumed that this constant value is the value at 0 K and it is designated as ρ_o .

The topic of most interest in recent years is the observed deviations from Matthiessen's Rule (DMR). The rule as usually seen, states that the phonon (intrinsic) resistivity of the pure solvent, ρ_p , and the impurity resistivity due to the solute, ρ_o , are additive, and that the latter contribution is independent of temperature. Therefore, the total resistivity, ρ , becomes

$$\rho(c, T) = \rho_p(T) + \rho_o(c) \quad (3.6)$$

over the entire temperature range (c is the impurity concentration). In general, defects and surfaces also contribute to ρ_o . It has been known almost since its presentation that the rule is not exact, but when one considers that it resulted from an experiment on dirty alloys at near room temperature in the 1860's, it has had an amazing success. The way to make an exact equation is to introduce a third term, Δ , the deviation term:

$$\rho(c, T) = \rho_p(T) + \rho_o(c) + \Delta(c, T) \quad (3.7)$$

It is the study of the behavior of Δ with impurity type and content and with temperature that is the major topic of interest today. Two excellent and very thorough reviews of the subject have been published by Bass [72] and by Cimberle, Bobel, and Rizzuto [73]. The first of these covers deviations due to various defects and size effects as well as impurities. A lengthy treatment of nickel-based alloys is presented by Yamashita and Hayakawa [74], and a discussion of size effect deviations is given by Boughton and Neighbor [75]. Figure 3.3, from Bass, shows the various behaviors observed for Δ from 0 K to room temperature. His assessment of the available data shows that: at low temperatures, Δ rises with temperature usually more slowly than $\rho_p(T)$, but often exceeds $\rho_p(T)$ in size near $\Theta_D/10$ (Θ_D is the Debye temperature). The hump which may occur at $\Theta_D/4$ to $\Theta_D/5$, moves to lower temperatures and increases in relative size as c decreases. For values of c greater than a few tenths of a percent, Δ can be represented by a constant plus a linear

term in T . Both of these terms are observed to vary linearly with c at constant temperatures. The term linear in T may either increase or decrease with temperature. At high temperatures, Δ is usually 5 to 10% of ρ_0 , but in some cases (cold worked noble-metal alloys and magnetic alloys) it has been observed to be equal to ρ_0 . Table 3.3 indicates alloy systems that have been studied for deviations from Matthiessen's Rule. Most of the information in the table comes from the two reviews mentioned above [72,73].

It is important to stress that, from a strictly technological point of view, these deviations are most often not large enough to be of concern.

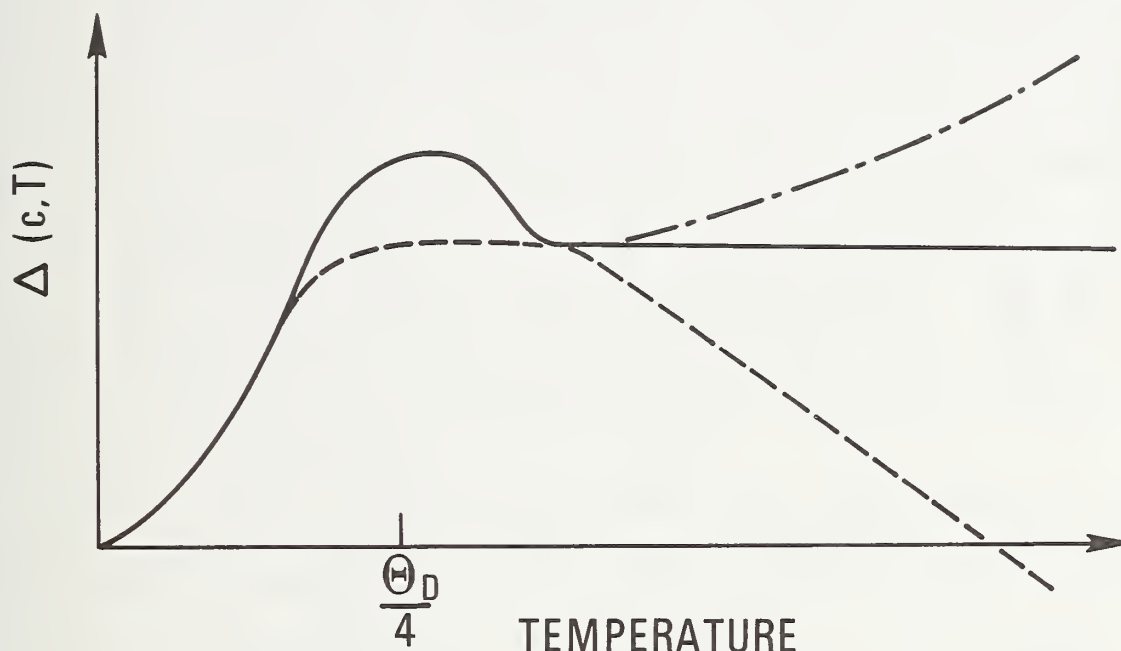


Figure 3.3. Types of behavior observed for deviations from Matthiessen's rule in alloys as a function of temperature [72].

Kondo effect. This low temperature phenomenon has been extensively investigated in recent years. The manifestation of the effect is a minimum in the electrical resistivity of pure metals and alloys containing dilute magnetic solutes. The classical material is CuFe, but the minimum has been observed in many other systems. The resistivity minima can occur at any temperature, but most systems show it in the range 2 to 30 K. Again, the effect is usually very small, although it can be a serious impediment to the creation of the constant resistance alloys for low temperature applications described in Chapter 4.

The effect arises as the result of an interaction between the magnetic moment of a localized impurity and the average moment of nearby conduction electrons. The review article by Daybell and Steyert [76] still represents the best compilation of information on the subject, although many papers have appeared since then.

Basically the interaction is thought to occur as follows: below a critical temperature, T_k , a "quasi-bound state" forms between the moments, characterized by an antiferromagnetic exchange interaction in these alloys, i.e., the conduction electron spins shield

the impurity moment. The temperature T_k depends exponentially on the exchange constant J , so that very small changes in J can cause large variations in T_k . Values for T_k have been observed over five orders of magnitude for various transition elements in copper. For

Table 3.3. Alloy systems on which studies of deviations from Matthiessen's rule have been made

	SOLVENT METAL																									
	Ag	Al ^a	Au	Be	Cd	Co	Cr	Cs	Cu	Fe	Ga	In	K	Li	Mg	Ni	Na	Pb	Pd	Pt	Sn	W	Zn			
Ag		X	X		X									X	X										X	
Al	X		X						X	X					X										X	
As	X								X																	
Au	X	X							X	X						X				X						
Bi	X																				X					
Cd	X														X			X			X					
Ce															X											
Co		X	X			X			X	X						X										
Cr		X	X			X			X	X						X										
Cu	X	X	X													X										
Er																		X								
Fe		X	X			X			X							X										
Ga		X																								
Gd															X											
Ge		X							X	X																
Hf						X										X										
Hg														X												
In	X		X						X		X				X			X			X					
Ir						X										X										
Li															X											
Mg	X	X			X									X												
Mn		X	X			X			X	X					X	X										
Mo						X				X						X										
Nb						X	X									X										
Nd															X											
Ni			X						X	X																
Os						X				X						X										
Pb															X											
Pd	X		X						X							X										
Pt	X		X						X							X										
Re						X			X							X										
Rh			X			X										X				X						
Ru						X			X							X										
Sb	X								X						X							X				
Si									X	X					X											
Sn	X		X						X	X	X	X			X											
Ta		X				X	X			X						X										
Ti						X				X						X										
Tl															X											
V		X				X	X			X						X										
W						X				X						X										
Zn		X	X						X						X										X	
Zr		X	X			X										X										

^aData on solvents printed in italics are available with unknown solute elements in some instances.

iron, the temperature is most likely around 30 K -- its determination is not as straightforward experimentally as it is theoretically. It is interesting that the experimental effects of this quasi-bound state were known for many years before the successful theoretical treatment by Kondo [77]. The effect of this interaction on the resistivity is to cause an increase in the resistive contribution per impurity, $\Delta\rho/c$, as the quasi-bound state forms, i.e., as the temperature is lowered. This is not a sharp step, but the value of $\Delta\rho/c$ is constant above and below it. The step height is considered to be impurity independent and has a value ~ 0.14 n Ω cm/at. ppm for copper-based alloys. The effect of this step on the measured (i.e., total) resistivity of the metal is to give the observed minimum in the resistivity versus temperature curve of the alloy at near T_K . It is interesting that this Kondo minimum is seen in nearly all "pure" copper -- indicative of its rather high iron content. Internal oxidation of the iron impurities in copper as described below, removes the Kondo minimum entirely. Also, a temporary breakup of the quasi-bound state can be caused by application of a strong magnetic field.

Gases as impurities. Gases occur to a limited extent as elemental impurities in metals. Oxygen is the most common. It occurs, for example, even in "oxygen free" copper at 10-20 ppm. Gas analysis is very difficult at these levels and the content is seldom stated by the supplier. The contribution to the resistivity is of the same order as that of metallic impurities. As an example, Hess and Pawlek [78] report a value of 5.3 $\mu\Omega$ cm/at.% for oxygen in copper.

Nitrogen is added as a strengthening element in various modern stainless steels that are used extensively for low temperature structures. Almost no data exist on the effect of this addition on the resistivity, but one would expect it to give only a small contribution to the already very high values for these metals.

Hydrogen in metals causes serious embrittlement problems. It is not a naturally occurring impurity, but often is encountered in high temperature industrial processes. Analysis of hydrogen content is very difficult and essentially no low temperature specific resistivity data exist.

Thin films of alloys of alkali metals with rare gases have been made to study the physics of metal-insulator transitions [79]. At low impurity levels, the contribution to the low temperature resistivity is normal (2.2 $\mu\Omega$ cm/at.% for krypton in rubidium and 2.8 $\mu\Omega$ cm/at.% for xenon in cerium). At ~ 40 at.% gas the resistivity at 7 K is only ~ 100 $\mu\Omega$ cm for both alloys, but at high percentages of the gas (>75 at.%), the resistivity exceeds 10^7 $\mu\Omega$ cm.

The addition of specific gases under controlled conditions of temperature and pressure can be used to greatly decrease the low temperature resistivity of metals. The major application of the technique has been to effectively remove the residual iron from copper. This is accomplished by causing the oxygen to form compounds with the iron, primarily Fe_3O_4 , which agglomerate as relatively large particles even in very dilute alloys (<4 ppm Fe). By this technique, copper single crystals with residual resistivity ratios near 65 000 and polycrystalline wires with ratios of 20 000 have been produced. These ratios are much higher than the approximately 2000 ratio of the highest purity unoxidized copper.

The efficacy of the technique is illustrated in figure 3.4, which shows the results of 4 K resistivity measurements on a series of dilute CuFe alloys [80]. Internal oxidation has also been used to increase the residual resistivity ratio of gold, silver, and tantalum. The techniques and a historical review have been published by the author [81].

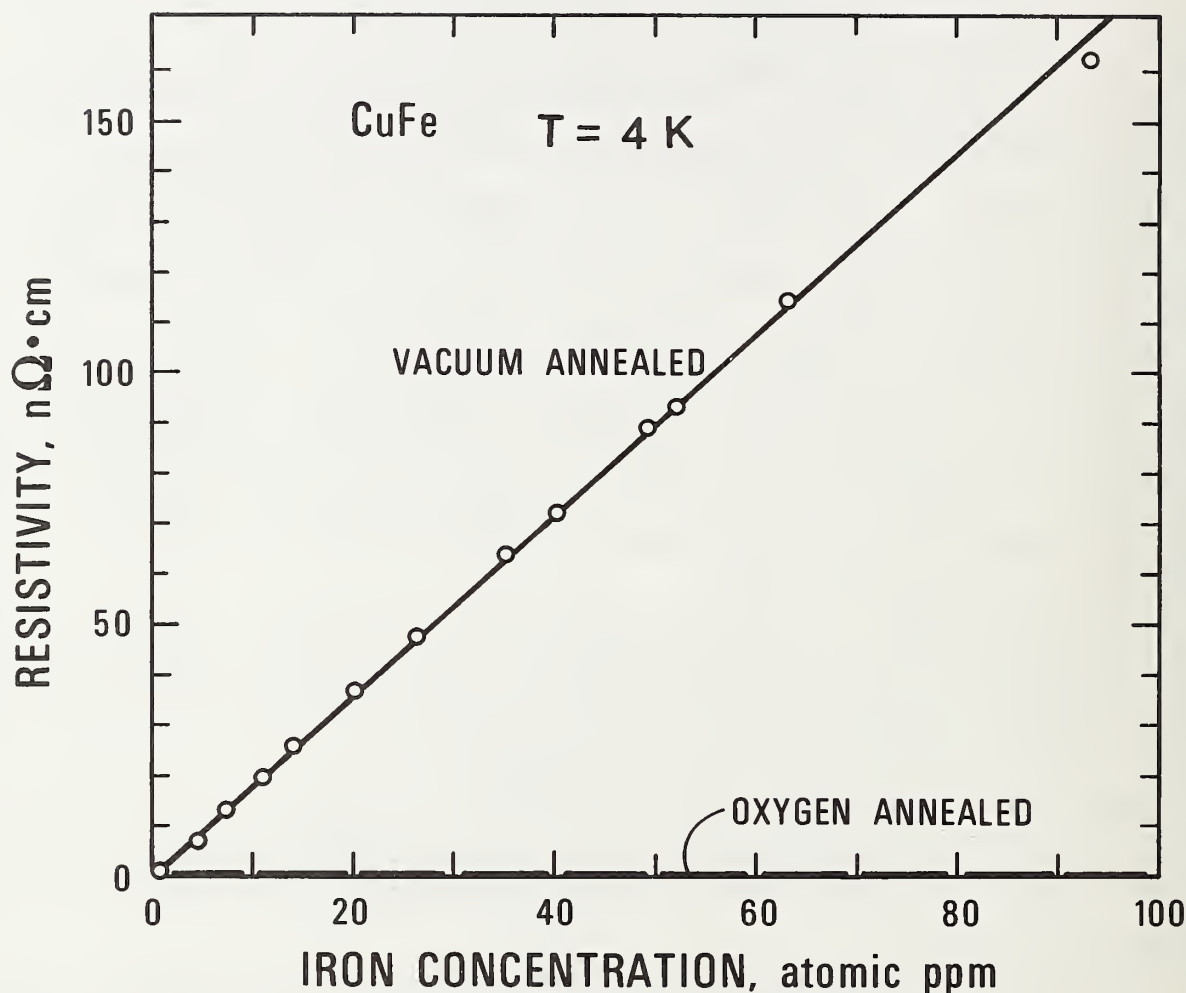


Figure 3.4. Electrical resistivity of CuFe alloys before and after internal oxidation.

3.3 Defect resistivity

Defects in crystal structure of metals and alloys can give significant contributions to the low temperature resistivity. In some metals, the available purity is such that defects represent the major contribution to the residual resistivity. The simple act of winding a wire around a sample holder can decrease the residual resistivity ratio by a factor of two or more. Defect resistivity is a topic dear to the heart of theorists, and many texts, such as Ziman [82], go into great detail on the calculation of the contributions of the various defect types. Here we present a brief description of the defects, some comments on how they are introduced into metals, and the resistivity modifications that they cause.

The resistive contribution of most defects is not strongly temperature dependent, although deviations from Matthiessen's Rule (mentioned above) do occur. Temperature still plays an important role, however. Defects formed at 4 K tend to stay put in the lattice, but as the temperature is raised, the various types start to anneal out, giving a so-called recovery curve for the defect resistivity. This recovery usually starts well below room temperature.

Defects and their production. Defects are usually grouped according to their dimensionality. The principal point defects are vacancies and interstitials. The term interstitial refers to an atom of the host lattice located off a normal lattice site. Other atoms, notably gases, may also exist in interstitial positions. Depending on the method of production, vacancies can occur alone (Schottky defects) or in vacancy-interstitial pairs (Frenkel defects). The former are found primarily in quenched specimens, and the latter in irradiated specimens. The literature on these defects is enormous. The book by Seeger, Schumacher, Shilling, and Diehl [83] is suggested as a starting point. Direct experimental determination of defect concentrations is not possible. Typical experimental values quoted are in the range 0.01 to 0.1 at.%. The topic of radiation damage effects in metals is one of great interest, both at high temperatures, because of fission reactor problems, and at very low temperatures, because of the use of pure metals to protect (stabilize) superconductors in fusion devices [84]. Point defects are the first to anneal out of a metal with increasing temperature and the annealing may start at temperatures as low as ~ 10 K.

Dislocations are line defects, but their usual configuration involves loops, clusters, and tangles. Creating and measuring a known concentration of dislocations in a metal is very difficult. The units of dislocation density are lines per square centimeter, or cm^{-2} . Dislocations occur naturally in all real metals, and their concentration can be increased somewhat by quenching and increased a great amount by deformation. In annealed aluminum or copper, for example, the dislocation density tends to be $\sim 10^6$ lines/ cm^2 , although with care densities many orders of magnitude lower can be achieved. After severe deformation, this number may reach 10^{12} lines/ cm^2 . There is a massive amount of literature on this topic also. Nabarro [85] discusses all aspects of dislocations and includes a brief section on their effect on electrical properties. Dislocations are relatively difficult to anneal out of metals and, in most common metals, temperatures well above room temperature are necessary for complete recovery.

The common planar defects are stacking faults and grain boundaries. Stacking faults occur in conjunction with dislocations and, in fact, their existence was first proposed to account for discrepancies observed between theory and experiment on dislocation resistivity in fcc metals. The units of stacking fault (and grain boundary) density are those of surface area per unit volume or cm^{-1} . Stacking faults are most often introduced by quenching, although deformation will also suffice. In an annealed metal, their density tends to be less than a few hundred inverse centimeters. Both Nabarro [85] and Ziman [82] present extensive discussions of stacking faults.

The important parameter for grain boundary resistivity is the boundary area per unit volume or S/V . The determination of S/V from observation of a single surface of a speci-

men is not entirely straightforward with any of the several existing techniques. Grain size in metals can cover the range from a few tens of micrometers to many centimeters leading to S/V values of 10 to 1000 cm^{-1} . The introduction of controlled grain sizes in pure metals is usually performed by deformation followed by recrystallization and subsequent grain growth. Specimen size limits the maximum grain size achievable in most pure metals. Pure aluminum wires, for example, will grow a "bamboo" structure of grains about the size of the wire diameter, whereas in copper the grains tend to be somewhat smaller and randomly located.

It should be reemphasized that the measurement of defect density is not at all simple for any of the defect types and errors of a factor of 2 or 3 may occur. The separate defect types never have the courtesy to appear alone and separation of the resistive contributions is also a significant source of uncertainty. Furthermore, the presence of impurity elements may have an effect on the type and number of defects introduced by a particular procedure.

The resistive contribution of defects. From a theoretical point of view, the problem in calculating the resistivity contribution from isolated defects is the evaluation of what fraction of the resistivity is due to the core of the defect and what fraction is due to the surrounding strain field. There is very little agreement among authors. When the more realistic case of combined defects, such as dislocation loops containing stacking faults, is considered, the relative contribution of each defect type becomes a matter for debate, again with little agreement. When very large numbers of defects are introduced, such as in dislocation tangles, the contribution per unit defect is expected to decrease. One point on which all theoretical calculations agree is that the scattering from the extended defects is anisotropic and has at least some component that gives small angle scattering [86]. Because of this, the resistivity contribution should be somewhat temperature dependent and this, indeed, appears to be the case experimentally. A further impediment to theory-experiment correlation is the refusal of the defects to occur in the same form from one experiment to the next. Linear dislocations and dislocation loops containing stacking faults are most common. The stacking faults may, however, occur as three-dimensional defects, such as multilayers or, at least in copper, as tetrahedra. Special conditions may also produce helical dislocations or other configurations. The general conclusion is that the best available theoretical calculations agree with experiment to within an order of magnitude.

The experimentally determined vacancy resistivities reported for aluminum center around $2.6\text{ }\mu\Omega\text{ cm/at.}\%$ with about a 40% spread [3], and Blatt [70] suggests a value of 1.0 to $1.5\text{ }\mu\Omega\text{ cm/at.}\%$ for copper. In each case the interstitial resistivity appears to be about 1/2 to 2/3 of the value for vacancies. Theoretical copper values reported by Welles [69] are 0.4 to $1.8\text{ }\mu\Omega\text{ cm/at.}\%$ for vacancies and 0.2 to $10.5\text{ }\mu\Omega\text{ cm/at.}\%$ for interstitials!

Experimental dislocation resistivities in both aluminum and copper tend to be $3 \pm 1 \times 10^{-13}\text{ }\mu\Omega\text{ cm}^3$, with the lower limit applying at 4 K. Note that multiplication by the dislocation density is necessary to obtain an actual resistivity. Again, there is a

wide variation of values ranging from 0.2 to $9 \times 10^{-13} \mu\Omega \text{ cm}^3$ found in the literature on aluminum. Values for several other metals are given in table 3.4.

Data on stacking fault resistivities are not as plentiful. The value for aluminum is apparently 2 to $5 \times 10^{-7} \mu\Omega \text{ cm}^2$, and that for copper, 10^{-6} to $10^{-5} \mu\Omega \text{ cm}^2$. The lower value is usually more appropriate at 4 K , but it is not the temperature dependence that is responsible for the range of the data. Again, determination of an actual resistivity requires multiplication by the stacking fault density.

Grain boundary resistivity values have been measured only occasionally [88] and disagreement over the proper method of determining S/V for bulk specimens puts any measurement in doubt by at least a factor of two. For copper and aluminum the contribution appears to be $10^{-6} \mu\Omega \text{ cm}^2$. Multiplication by S/V (in cm^{-1}) is necessary to derive a true resistivity. Room temperature values appear to be about 20% higher than those at 4 K .

Table 3.4. Dislocation resistivity in metals^a.

Material	Dislocation Resistivity ($\mu\Omega \text{ cm}^3$)
Ag	$3.4, 2.0 \times 10^{-13}$
Au	3.5×10^{-13}
Ni	9.4×10^{-13}
Fe	20×10^{-13}
K	4×10^{-13}
α -brass	18×10^{-13}

a. Data compiled by Barbee [8] from the literature.

3.5 Size effects

The increasing applications of very pure metals to cryogenic magnet construction brings the consideration of size effects very much into the realm of technology. Very pure aluminum and copper conductors may have electron mean free paths on the order of a millimeter and, since many conductors are of this size, better than half of the resistivity at low temperatures would be due to boundary scattering. Many new applications are being found for conducting composites, both as commercial superconductors and as high strength-high conductivity normal metals. In these materials, the interfiber spacing may be such that scattering of the electrons from the boundaries has a significant effect on the resistance. Also, new uses are being found for classical thin metal films of μm size in deposited circuits, very low temperature thermometry, and more exotic applications, such as dc transformers, that make use of the superconducting properties of aluminum films. Here we will concentrate on the relatively large conductors.

The general topic of dc size effects in metals is the subject of an excellent review by Brandli and Olsen [89]. Three parameters appear at least implicitly in all dc size effects theories: the ratio $K = d/\ell_b$, of the characteristic specimen dimension to the bulk electronic mean free path; the specularly parameter, p , which is the fraction of electrons specularly reflected from the surface; and the product $\rho_b \ell_b$ for the bulk metal, which should be a constant independent of size or temperature. This product is given in free electron theory by

$$\rho_b \ell_b = mv_f^2 / e^2 n \quad (3.8)$$

where n is the free electron concentration, v_f is the Fermi velocity, and e and m are the electronic charge and mass, respectively. If one considers the real Fermi surface of a metal, one arrives at a more realistic (and more complex) form for the conductivity in terms of an integral over the surface of the momentum-dependent mean free path. The simpler expression above will suffice for our purposes. Also, in the following presentation p is assumed to be zero, corresponding to diffuse scattering at the surface. The exact value of p and its dependence on various parameters is a topic on which there is considerable debate. The experimental literature indicates that zero is as good a value as any for calculating correction terms, particularly when one considers the uncertainties in the other parameters.

The parameter $\rho_b \ell_b$ is not truly temperature independent for real metals, i.e., deviations from Matthiessen's rule occur [75]. Furthermore, the value determined by different types of experiments is highly variable. Brandli and Olsen [89] list values of $\rho_b \ell_b$ for a variety of pure metals. These vary from 3.5 to $68 \times 10^{-12} \Omega \text{ cm}^2$, with most between 6 and $20 \times 10^{-12} \Omega \text{ cm}^2$. Values of $6.0 \times 10^{-12} \Omega \text{ cm}^2$ for aluminum and $6.6 \times 10^{-12} \Omega \text{ cm}^2$ for copper at 4 K are representative of the literature. Use of this number is really the only easy method of determining the electron mean free path.

There are many formulas available in the literature for calculating the size effect resistivity. The earliest relationships, which prove to be adequate in most instances, are due to a suggestion of Nordheim [90] for wires

$$\rho/\rho_b = 1 + 1/K \quad (3.9)$$

and the Fuchs [91] relationships for films, which like most of their descendants, can be written simply only in the extreme limits of K ($= d/\ell_b$). The equations, in terms of conductivity are

$$\sigma/\sigma_b \approx 0.75 K \ln K^{-1}, \quad K \ll 1 \quad (3.10)$$

$$\sigma/\sigma_b \approx 1 - 3/8 K \quad K \gg 1 \quad (3.11)$$

The specularly parameter, p , appears in the more general form of these equations, but here it has been set to zero as discussed above.

Size effects can be of importance in the world of low temperature conductor applications. Figure 3.5 shows the measured versus the bulk residual resistivity ratio for copper wires of quite reasonable size. One should also note that a magnetic field applied to a metal showing a significant size effect may cause a dramatic decrease in the measured low temperature resistivity [89].

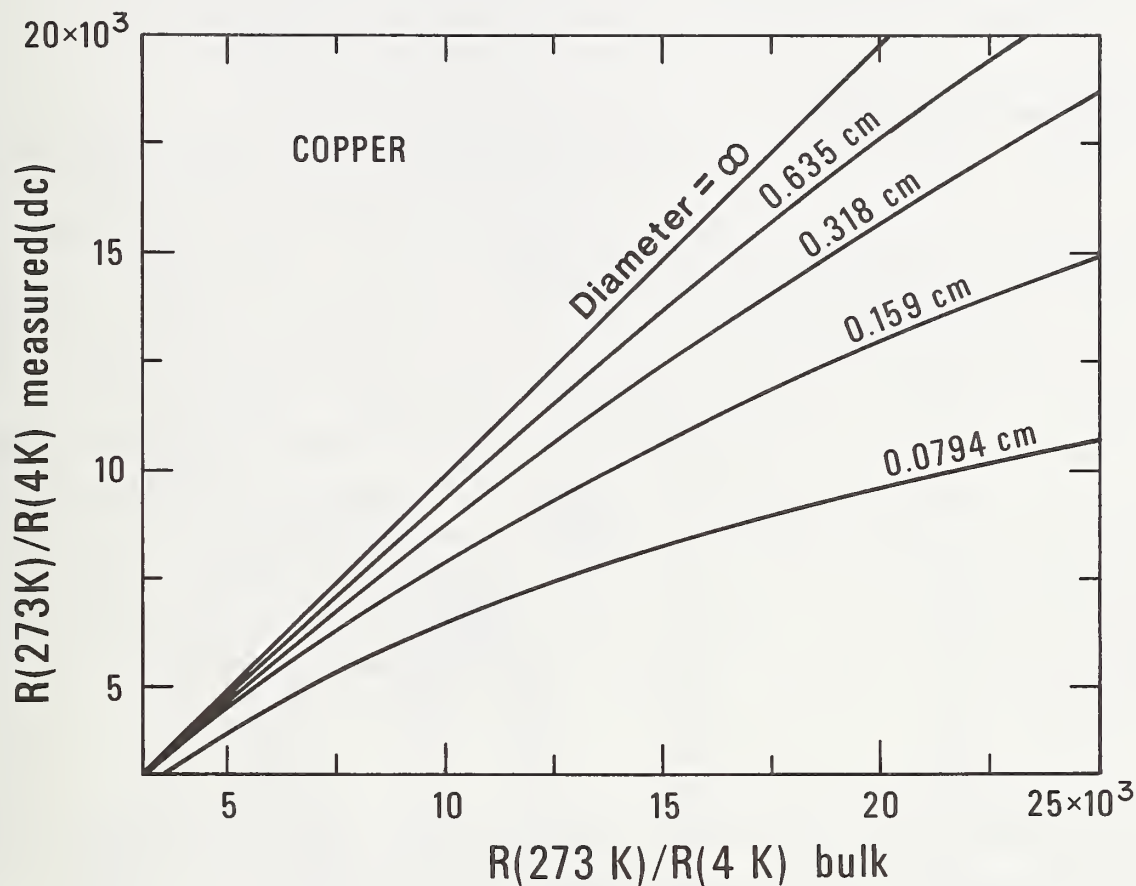


Figure 3.5. Measured versus bulk residual resistance ratio for copper wires of various sizes. Calculation uses $(\rho l)_{\text{bulk}} = 0.66 \times 10^{-11} \Omega \text{ cm}^2$.

Chapter 4. ALLOY RESISTIVITY

The alloys of concern here are the nondilute mixtures of metals. In almost all of these alloys, the lattice resistivity is significantly smaller than the temperature-independent components and, thus, there is often not much difference between the resistivity measured at room temperature and that measured near 4 K. In general, however, the variety of behavior exhibited by alloys is astonishing in its diversity.

4.1 Well-behaved alloys

As anyone familiar with the workings of Murphy's Law might predict, there are few alloys that fall into this category. In the most classic cases, such as AgAu and CuAu, the component metals are mutually soluble across the entire range of composition. The resistive behavior of these two alloys is shown in figure 4.1 (from Bardeen [92], reporting earlier data) and figure 4.2 [93] respectively. Apparently no recent measurements covering the entire composition range have been made on any binary alloy system. Bardeen also presents curves from the early literature showing similar behavior for InPb, PtPd and KRb. These alloys are homogeneous solid solutions with a random distribution of atoms. As figure 4.1 implies, the soluble, non-ordered alloys have both a temperature dependent and a residual contribution to their resistivity. The residual resistivity ratio over the mid-range compositions is not large. A recent measurement on an Ag25%Au alloy [94] gave $RRR = 1.3$ and it looks from figure 4.1 like this value is roughly maintained over the entire mid-range. The residual resistivity can be described by Nordheim's rule

$$\rho_0 \propto x(1 - x) \quad (4.1)$$

where x represents the fraction of one of the constituent atoms. Note that the resistance change with composition is very large even for these simple alloys.

Other alloys that fall in the well behaved category are those with a solid solution phase which covers a relatively large range of composition. Of the technically important metals, the CuZn alloys containing ~ 35 wt.% Zn are in this class. These are the classical brasses. Figure 4.3 is from the data of Henry and Schroeder [95] on alloys made from pure copper ($RRR \sim 1300$). The resistivity ratio here is also quite small above a few percent zinc. Their figure 6 shows a linear temperature dependence of the resistivity for all the alloys above 40 to 50 K.

Another system, not strictly an alloy, that exhibits uncomplicated resistive behavior is heterogeneous mixtures of mutually insoluble metals, such as PbZn or ZnCd, in which the two elements each form small crystallites. The resistivity is an average of values for the two pure metals and is monotonic across the composition range - it is not often linear. The temperature dependence should also, of course, be an average. The PbSn solders are of this type, but the solid is more complex, consisting of a eutectic mixture (also found in ZnCd) and crystallites of lead with up to 25% Sn at the lead-rich end. Regardless, the observed resistive behavior is as stated above.

Figure 4.1. Resistivity of the well-behaved alloy system AgAu [92].

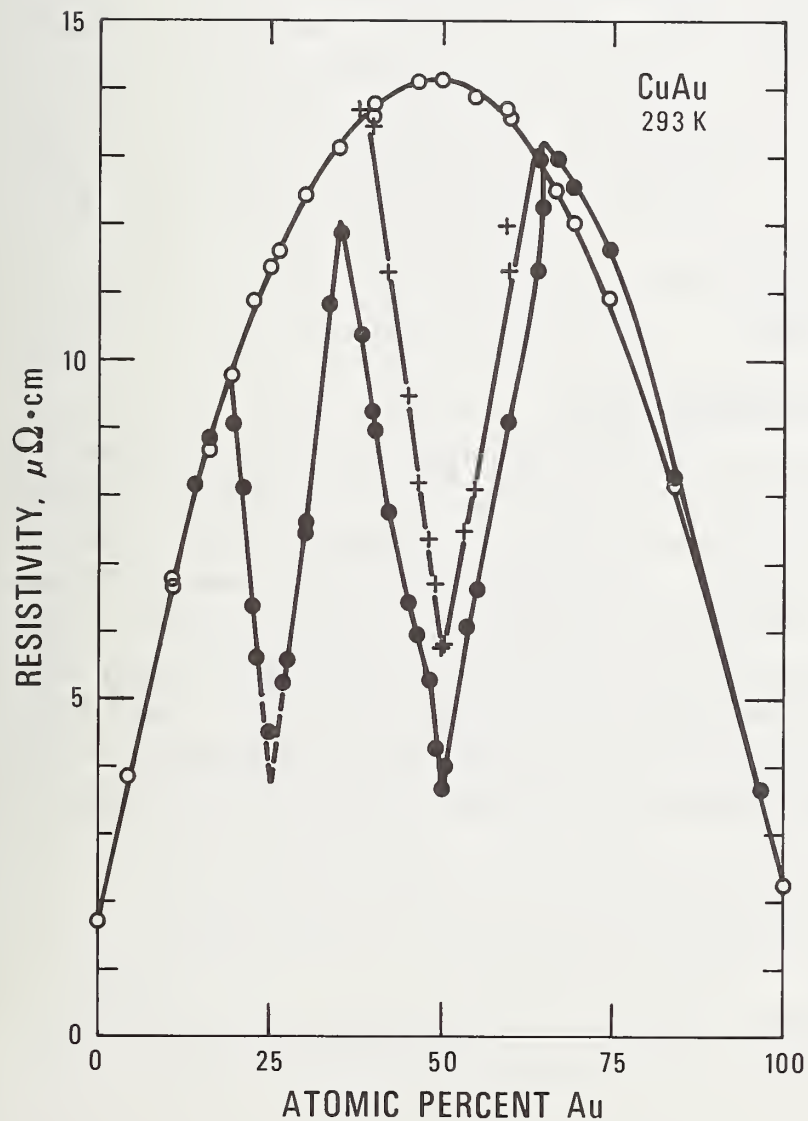
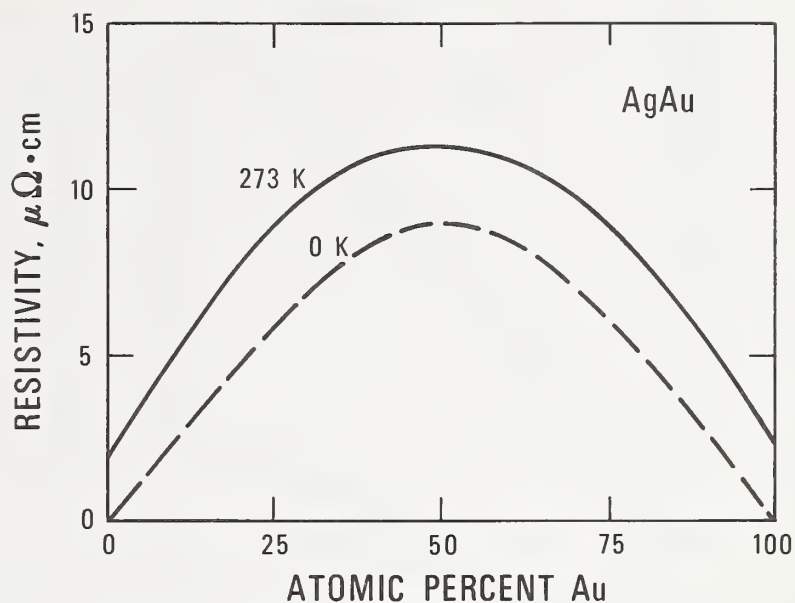


Figure 4.2. Resistivity at 20°C of the alloy system CuAu. Open circles are from the well-behaved disordered alloy quenched from 650°C. The closed circles show the effect of ordering introduced by a 200°C anneal, and the +, the effect of a furnace-cool of the alloys [93].

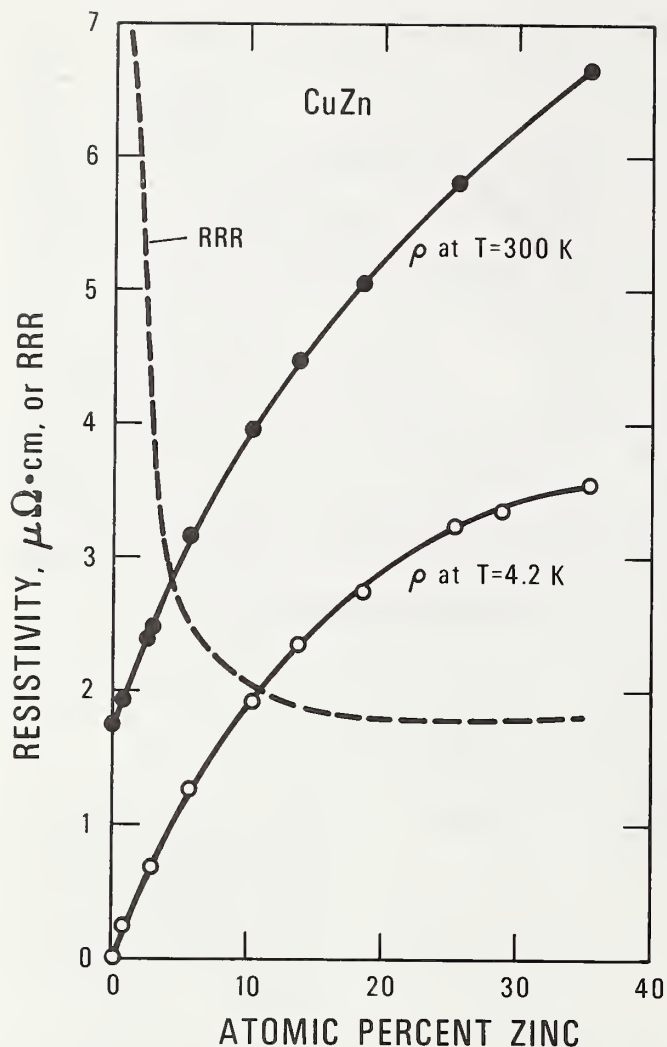


Figure 4.3. Behavior of the α -phase resistivity of brass [95].

4.2 Alloys with ordering and amorphous alloys

Some disordered binary alloys can be ordered by annealing well above room temperature. When this occurs, the two types of atoms each form their own separate crystallographic structure within the alloy. Thus, the A atoms will be preferentially located in one sublattice and the B atoms in another. This ordering results in a lowering of the resistivity at all temperatures. The classical alloy system in this group is CuAu. The effect of ordering on the resistivity is shown in figure 4.2. The highest degree of ordering occurs at the compositions CuAu and Cu_3Au ¹. The existence of the ordered sublattices has been confirmed by x-ray techniques. To the best of our knowledge, there are no alloys which undergo this type of ordering below room temperature - certainly none of technological importance.

¹These are not intermetallic compounds. They do not precipitate from the alloy and they do not have a high resistivity.

As one might expect, the resistivities of ordered alloys show a greater temperature dependence than do their disordered counterparts. There is only a limited amount of information available on this topic. Cohen and Bever [96] report $RRR = 4.0$ ($\rho = 4.27 \mu\Omega \text{ cm}$ at 293 K) for ordered Cu_3Au and $RRR = 1.2$ ($\rho = 11.32 \mu\Omega \text{ cm}$ at 293 K) for the disordered alloy. The latter value is also indicated by the data of Varotto and Vidoz [97]. Similar ordering behavior was observed in alloys of AgMg by Gangulee and Bever [98] with RRR values ~ 13 for ordered AgMg . There is no listing in the literature of alloys which exhibit ordering. The most comprehensive treatment is not very recent [99]. The general field of order-disorder phenomena is reviewed by Guttman [100]. Low temperature data have been reported for NiFe ($>65 \text{ at.}\% \text{Ni}$), CuPt , $\beta \text{ AgZn}$, $\beta \text{ AgCd}$, and $\beta \text{ brass}$. In the last three materials, the occurrence of other alloy phases tends to complicate any attempt to observe the ordering [101].

Alloys of the form Au_4X , where X stands for various transition elements, have been studied [102,103]. These alloys show both an atomic ordering at high temperature and a magnetic ordering, which usually occurs below room temperature. The resistivity always decreases below room temperature with a change to a steeper slope below the magnetic transition. According to Toth et al. [102] residual resistance ratios tend to be around 2 to 3 and the alloy resistivities at 4 K vary from $\sim 5 \mu\Omega \text{ cm}$ for Au_4Mn to $145 \mu\Omega \text{ cm}$ for Au_4V . On the other hand, Maple and Luo [103] report $95 \mu\Omega \text{ cm}$ at 4 K ($RRR = 1.7$) for the ordered alloy Au_4V . The same alloy in the disordered state shows a slowly increasing resistance with decreasing temperature to about 40 K, followed by a slight decrease to 4 K ($\rho = 217.5 \mu\Omega \text{ cm}$ at 4 K, $RRR = 0.96$).

Amorphous alloys are generally thin films deposited on cold substrates. Much of the existing work has been done on semiconducting or magnetic alloys, usually containing at least one nonmetallic component. The temperature and magnetic field dependence of the resistivity of a number of these alloys are reported by Cochrane and Strom-Olsen [104]. Measurements on the low temperature resistivity of amorphous binary metallic alloys have been made by Korn and co-workers. A review of the work on alloys of gallium, tin, lead, and bismuth with the noble metals is given by Korn, Pfieffe, and Zibold [105]. Nearly all such alloys have high resistivities (~ 50 to $150 \mu\Omega \text{ cm}$ at 4 K) and residual resistivity ratios close to unity. The resistivity may rise or fall with decreasing temperature depending on the alloy makeup and the specific elements involved: amorphous CuSn alloys show a resistivity drop with decreasing temperature below 40% Cu, a peak at near 40 K for 40 to 60% Cu, and a rise at higher values. The residual resistivity increases with increasing copper content. A more recent paper [106] describes measurements on amorphous CuFe alloy films covering the entire composition range. Residual resistivities range from $16 \mu\Omega \text{ cm}$ for unalloyed copper to a peak of $\sim 205 \mu\Omega \text{ cm}$ at 80% Fe. The slope of the ρ -T curve is always positive and is low up to $\sim 10\%$ Fe but then increases sharply to a maximum at $\sim 30\%$ Fe.

4.3 Alloys with phase transitions or precipitation

A large number of alloys, both ferrous and nonferrous, undergo phase transformations below room temperature. These are usually martensitic transformations and the resulting material is called martensite. The transformations are a diffusionless shear type and the resulting martensite takes the form of plates, sheets, and needles, with an accompanying macroscopic shape change or change in surface relief. The transformation may occur spontaneously upon cooling below a characteristic temperature M_s , or it may be induced by stress below a characteristic temperature M_d . Thermally induced transformations are at least partially reversible, but often with a large hysteresis. Martensitic transformations are common in many materials of technological interest, such as stainless steels, brasses (β), titanium alloys, lithium, and sodium, to name only a few. The physics and metallurgy of the transformation are treated in many texts. A survey of the literature regarding specific low temperature transformations is given by Reed and Breedis [107].

With so many alloys involved, one shouldn't expect a great deal of uniformity in the resistive behavior and, in fact, that is what is observed. Quite a few materials, however, show resistance-temperature curves like those shown in figure 4.4 [108] for β -brass. The normal decrease of resistivity with temperature is interrupted by the transformation.

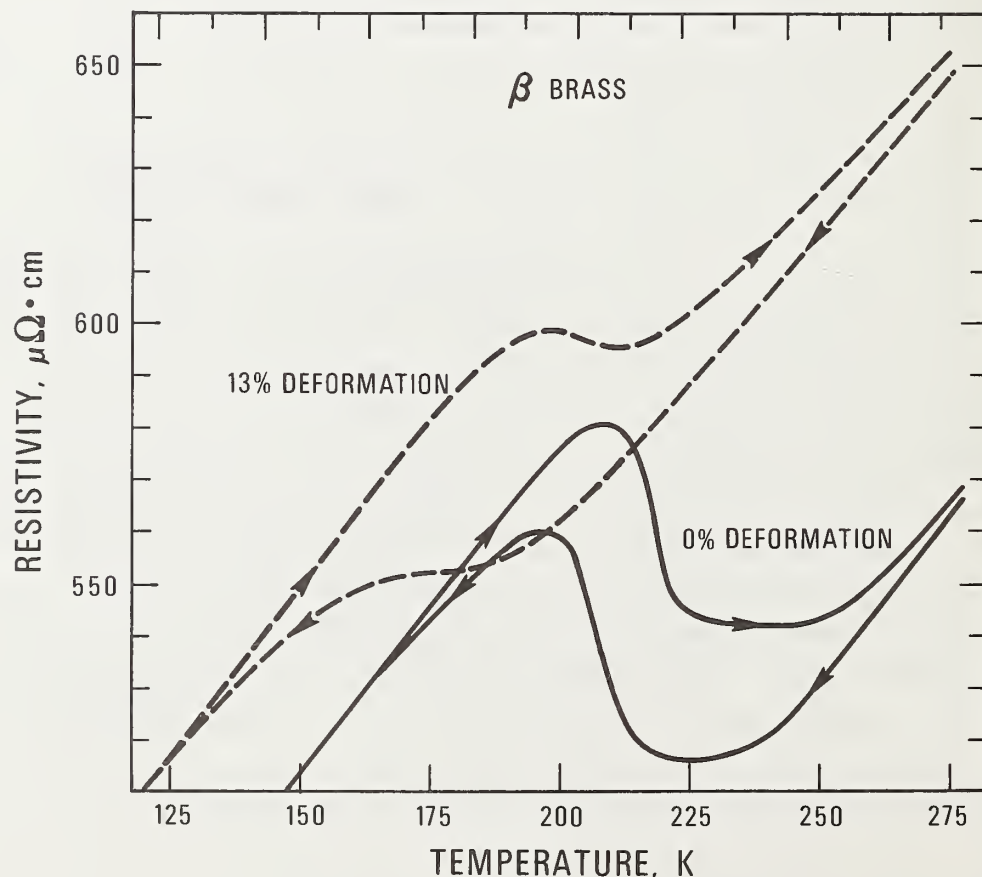


Figure 4.4. The effect of martensitic transformation on the resistivity of β brass [108].

The resistivity increases while the higher resistance martensite is forming, followed by a continuation of the decrease to the residual resistivity value (not reached in the experiment shown). The warming curves show the reversibility of the thermally induced martensite. The deformation martensite remains. Note that the resistivity values are quite high.

Another special group of alloys is that in which age-hardening occurs due to the slow precipitation of particles of a second phase relatively near room temperature. A number of commercial aluminum alloy are of this type. Whether the resistance initially increases or decreases upon isothermal annealing seems to depend on the temperature and, of course, on the material. Federighi and Cezesara [109] show both types of behavior for an Al 5% Mg alloy. The resistivity decreases on annealing at $T > 20^{\circ}\text{C}$ and increases for $T < 20^{\circ}\text{C}$ (down to -40°C). The increase in resistivity is taken as an indication of the formation of Guinier-Preston zones prior to the precipitation [110]. One would expect that the resistivity at all temperatures will ultimately decrease as the precipitation goes to completion, and this is implied by the isochronal annealing experiments by Federighi and Cezesara [109] as well as by Bardeen [92]. Low temperature resistivity data have been reported on AlZn, AlAg, AlCu, CuBe, and AlMn alloys.

4.4 Magnetic alloys

There are two groups of interest here: alloys in which a transition element is dissolved in a noble metal and the magnetic ferrous alloys, such as the steels. The alloys of the latter group usually show only a small temperature dependence of the resistivity; most often a slight decrease with decreasing temperature.

The magnetic alloys involving a noble metal and a transition element show ferromagnetic behavior at some concentration of the magnetic element. The Curie temperature is concentration dependent and may fall well below room temperature. Three alloy systems have been investigated in some detail: CuNi, AgPd, and AuNi. Of these, the first has been the most studied. The behavior of the resistivity with alloy concentration is still quite regular at all temperatures as shown in figure 4.5 and figure 4.6 and, as expected, the resistivity ratios are not high. They are highest for the ferromagnetic compositions. Within this range, however, a wide variety of behavior is observed as the temperature is decreased. The rate at which the resistivity drops with decreasing temperature always increases below the Curie temperature. This is illustrated by the CuNi data of Svensson [114], which has been quoted by nearly everyone, and that of Clinton, Tyler, and Luo [117] on AuNi, which shows Curie temperatures to below 4 K. The nonmagnetic alloys in these series show maxima and minima as well as general increases in resistivity with decreasing temperature [118]. Furthermore, the behavior of a given specimen may change with time of storage at room temperature [112] and is strongly affected by degree and type of deformation [119]. While very interesting from the viewpoint of metal physics, these varieties of behavior usually cause only a small relative change in the resistivity - on the order of several percent.

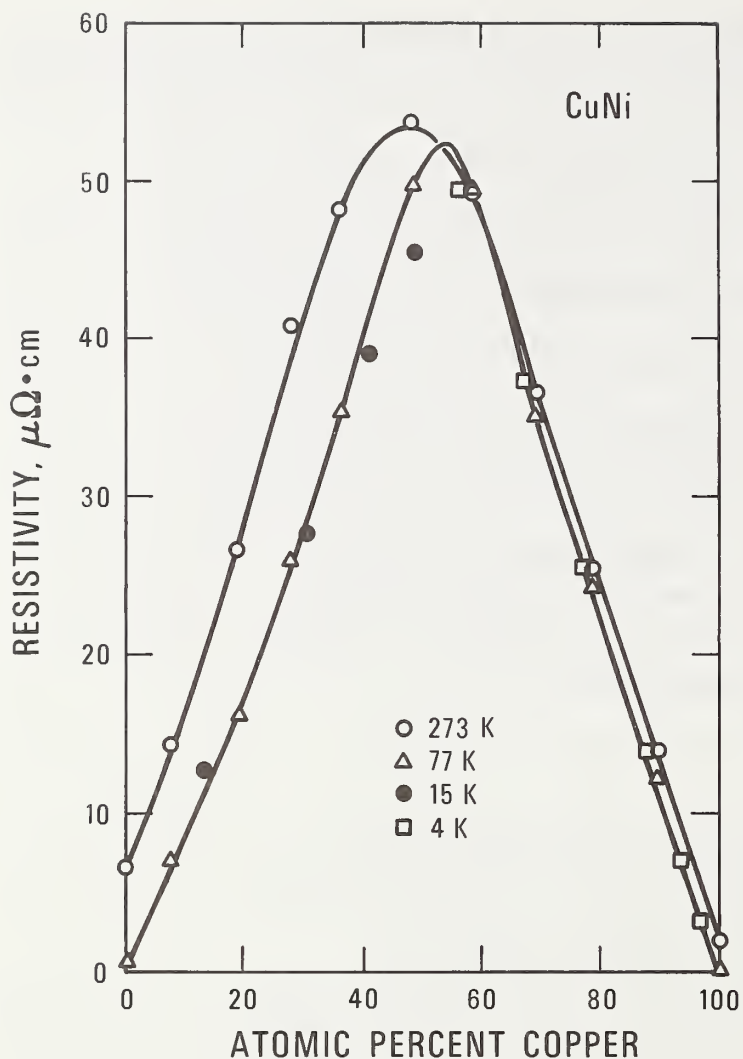
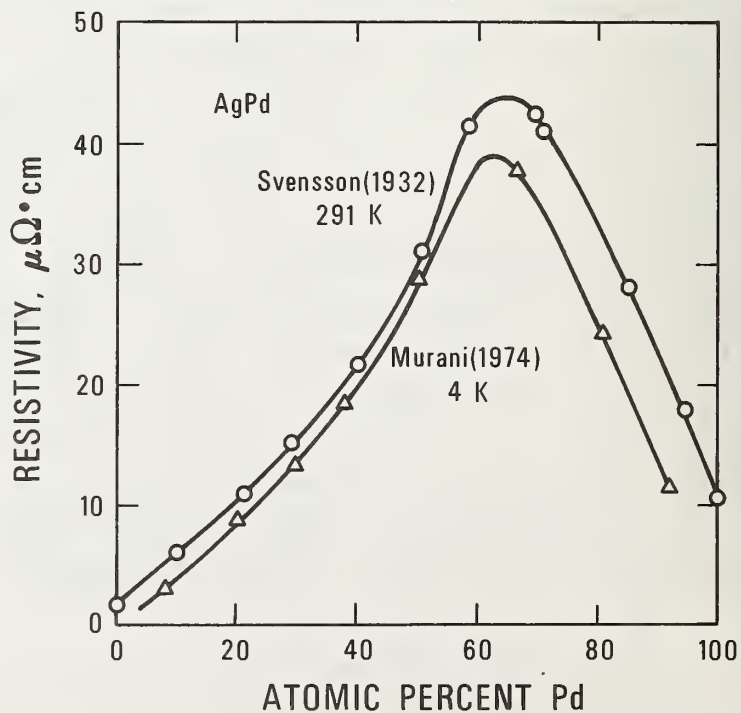


Figure 4.5.

The variation of resistivity with composition for the magnetic alloy CuNi. Legend: \circ , Δ and solid curves, Iguchi and Udagawa [111]; +, Legvold et al. [112]; \bullet , Krupkowski and de Haas [113]. Agreement with Svensson's [114] data is excellent.

Figure 4.6. The variation of resistivity with composition for the magnetic alloy AgPd. Sources of data are references [115] and [116].



4.5 Zero temperature-coefficient alloys

A surprisingly large number of low temperature applications require alloy wires that have been specifically designed for minimum resistivity variation over a certain range of temperature. For wires used in electrical heaters for calorimetry and thermal conductivity experiments, the entire range of temperature from 4 K to room is involved. A 1 to 5% variation in resistivity is acceptable. Wires used in temperature controllers for galvanomagnetic measurements, such as magnetoresistance, should be stable from 2 to 20 K, and should show as little variation with magnetic field strength as possible (see section 5.1). Variations of less than 2% are usually adequate. A wide range of new applications of the Josephson effect in voltage and current standards and comparators [120] requires resistance alloys with part-per-million (ppm) stability over a temperature range of a few degrees around 4 K. Magnetic field effects are frequently of concern in these devices. Finally, experiments at temperatures below 1 K often need special heaters with a low resistance coefficient. There is only limited information available in this very low temperature range. The paper by Cieloszyk, Cote, Salinger, and Williams [121] should be consulted for more information.

Materials usually employed for the room temperature to 4 K range tend to be the classical resistance alloys: constantan, manganin, nickel-chromium and others. Some of these alloys and their properties are described in table 4.1. These materials tend to have very high room temperature resistivities and to show very little change in resistance

Table 4.1. Low temperature properties of resistance wires

Wire	Nominal Composition (wt.%)	Nominal Resistivity at ~293K ($\mu\Omega$ cm)	Percent Change to 4 K (%)	Magnetoresistance $\Delta\rho/\rho$ at 4K and B (%)	References and Comments
Evanohm	75Ni,20Cr,2.5Al,2.5Cu	134 --- 76.4 128	-0.9 -0.76 -0.9(approx.) ---	--- --- 0 to 5 T +0.03-0.66 to 0.6T +0.23-0.83 to 18T	Furakawa, Reilly, and Saba [122] Hust [123] Lerner and Daunt [124] Woolam [125] Actual $\Delta\rho/\rho$ depends on sample
Karma	76Ni,20Cr,Fe,Al	133	-0.9	---	Furakawa, Reilly, and Saba [122]
Constantan	57Cu,43Ni	49 27.7	-6 -7	--- -4.6 to 5 T	Ibid. Lerner and Daunt [124]
Manganin	84Cu,12Mn,4Ni	48	-10	---	Furakawa, et al. [122]
NiCr	--	---	---	+0.002	Reported by: Cimberle, Michi, Mori, Rizzuto, Siri, and Vaccarone [126]
PtW	92Pt,8W (assumed wt.%)	66	-8	+0.024 to 9.5 T	Giauque, Lyon, Hornung, and Hopkins [127]. ρ and $\Delta\rho$ reported by Cimberle, Michi, et al. [126]
Silicon Bronze	96Cu,3Si,1Zn	28.3	-14	+0.005 to 14 T	Feldman, Talley, Rojeski, Vold, and Woolam [128]. CuSi is not a commercial alloy.
Phosphor Bronze	95Cu,5P	16.1	-23	+0.007 to 14 T	Ibid.

with decreasing temperature to about 250 K. Below that temperature, each alloy shows a decrease in resistivity, but the amount, as shown in the table, varies greatly. The magnetoresistance is small in nearly all instances. Its actual behavior with field varies from linear, with either sign, to quadratic to very complex, but there seems to be no significant dependence on the relative orientation of the magnetic field and the wire.

The alloys used for ppm stability applications near 4 K are quite different from the classical resistance alloys just described. They tend to be not as highly alloyed and, thus, have somewhat lower resistivities, on the order of 2 to 20 $\mu\Omega$ cm. Furthermore, most of the alloys are not available commercially. Copper- and aluminum-based alloys are most often used for a variety of reasons: (a) they tend to have shallow Kondo minima in their resistivity versus temperature curves in the region of interest due to natural or added magnetic impurities; (b) starting metal is available with the required high purity; (c) their magnetoresistance can be made quite small by proper alloying, and (d) they are materials that tend to be both strong and reasonably ductile, thereby facilitating the production of wire.

Investigation of aluminum-based alloys have been recently reported by Warnecke and Kose [129] and by Cimberle, Michi, et al. [126]. The first of these describes a commercial Al5Mg alloy showing a temperature coefficient of resistance (TCR) of $\sim 2 \times 10^{-7} \text{ K}^{-1}$ between 2 and 4 K. The remainder of the alloys exhibit TCR values below 10^{-4} K^{-1} over this range with many $\sim 10^{-6} \text{ K}^{-1}$. The magnetoresistance of the Al5Mg alloy at 4 K was $\sim 7 \times 10^4 \text{ T}^{-1}$, whereas the 10^{-6} K^{-1} alloys showed $\sim 7 \times 10^{-5} \text{ T}^{-1}$, both to high fields. At very low fields, $< 0.1 \text{ T}$, the sensitivity is apparently much smaller.

Three copper-based alloys have been investigated in detail: phosphor-bronze [126], CuGe [130], and silicon bronze [131]. The 2 to 4 K TCR values all are 2 to $4 \times 10^{-6} \text{ K}^{-1}$ (the CuGe and bronze TCR's are negative), and the silicon bronze magnetoresistance is $\sim 10^{-5} \text{ T}^{-1}$. Similar resistivity behavior has been reported for CuNi and CuPt alloy resistors by March and Thurley [132]. One of their CuNi alloys shows $\Delta\rho/\rho < 1 \times 10^{-6}$ between 1.5 and 4.2 K.

Chapter 5. EXTERNAL RESISTIVE MECHANISMS

Magnetic fields, pressure, and stress can have significant effects on resistivity. These effects appear stronger at low temperatures because the intrinsic (phonon) resistivity component is so small.

There are many ways in which a magnetic field can affect the transport properties of solids and each one of them has its own name. As a group they are termed galvanomagnetic properties. Blatt [70] lists 16 of these in his Table 7.7 and all solid state physics texts discuss at least some of them in great detail. Galvanomagnetic effects in the anisotropic metals are the subject of a recent review by Hurd [133]. From a low temperature electrical applications point of view, only magnetoresistance, Hall effect, and magnetothermopower are of interest and, of these, only the former is a common concern. Effects caused by time-varying magnetic fields are also important, but they are covered in Chapter 6.

The effect of hydrostatic pressure on the resistivity has been investigated for a large number of conductors. It is seldom a problem in applications, but we have included it here since questions sometimes arise. Stress, on the other hand is a serious problem in nearly all conductor applications. Fatigue effects, too, must often be considered.

5.1 Magnetoresistance

All nonmagnetic metals show an increase in electrical resistivity with increasing magnetic field. This magnetoresistance effect has been one of the most extensively studied of the transport properties and data exist on nearly all pure metals and a great many alloys. On copper alone there were some 60 papers published through 1972 and several more since then. The primary reason for the interest in this phenomenon is its ability to indicate the topology and connectivity of the Fermi surface from the transverse magnetoresistance (field applied normal to the electric current) of single crystals, and the anisotropy of the electron scattering from the longitudinal magnetoresistance. These measurements are invariably performed at liquid helium temperatures because the magnitude of the effects scales with the product $\omega\tau$ (ω is the cyclotron frequency and is proportional to the field, H ; τ is the relaxation time and scales roughly with ρ^{-1}). A low temperature experiment is necessary to achieve the required condition $\omega\tau > 1$ with real metal samples. These topics are covered in detail in most of the texts already mentioned.

Here the behavior of the magnetoresistance of polycrystalline metals used in various technical applications at low temperatures is the concern. These metals are used primarily as conductors of electricity; the highly alloyed metals used in structural applications usually show a negligible magnetoresistance. It should be stressed that magnetoresistance is a phenomenon which is of importance only at low temperature and only for pure metals. A measurable effect at 4 K, with the magnetic fields usually available, requires resistivity ratios on the order of 10 to 100 for the common metals.

The observed behavior of many polycrystalline metals can be described by an empirical rule developed by Kohler [134]. The mathematical form of the rule is:

$$\Delta\rho/\rho_0 = f(H/\rho_0) \quad (5.1)$$

where H is the applied field and ρ_0 is the resistivity at zero field. The function f for polycrystalline metals is single-valued, increases monotonically and depends only on the metal and the relative orientation of the field and current. Note that the magnetoresistance, therefore, does not depend on impurity content or temperature, except as they affect ρ_0 . Kohler diagrams are log-log plots of observed data. Usually the plot is of $\Delta\rho/\rho_0$ versus $H \cdot RR(T)$ where $RR(T)$ is the resistivity ratio $\rho(273\text{ K})/\rho(T)$. When a number of metals are compared, a reduced Kohler plot is often used in which $\rho(273\text{ K})$ is replaced by the resistivity at the Debye temperature. One such plot, which has appeared in nearly every review (see Fig. 46 of [1]) presents data for a large number of metals. The data are quite old and a reevaluation is needed, but the general behavior is as predicted.

Copper shows an amazing degree of agreement with Kohler's rule. A plot made from the author's data [6] is shown as figure 5.1. The 200 data points used represent temperature from 4 to 20 K, fields to 9 T, and residual resistivity ratios from 10 to 10000. There is some evidence that extended defects, with their temperature dependent resistivity, may cause deviations from this plot. Also, radiation damage studies have shown deviations, especially at low fields [135]. Note that field-induced resistance increases by a factor of 100 are possible in very pure copper!

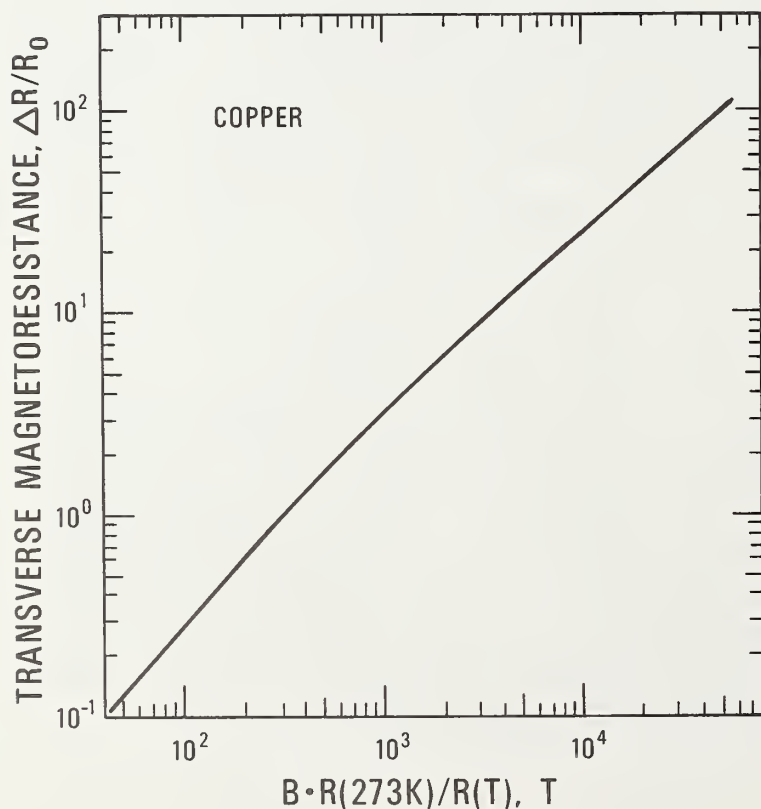


Figure 5.1. Kohler plot for the transverse magnetoresistance of copper.

Aluminum shows no inclination to obey Kohler's rule [136] for a wide range of parameters. The resistivity rises and then nearly saturates as the field is increased. At a given field $\Delta\rho/\rho_0$ shows a peak with increasing temperature at near 20 K. Maximum values of $\Delta\rho/\rho_0$ run from 0.5 to 5, far below those observed for copper.

Some general comments: Nearly any polycrystalline metal will show some agreement with Kohler's rule over a small purity range and at fixed temperature, and the Kohler plot will be linear. Very few metals show agreement when wide ranges of temperature, purity, defect concentration, and field are used. The longitudinal magnetoresistance of a given sample is always lower than the transverse, usually by a factor of two or more. The longitudinal magnetoresistance always saturates with increasing field. Samples whose dimensions are on the order of the electron mean free path or smaller will show a decrease in resistance with applied magnetic field. Ferromagnetic metals and alloys frequently show a decrease in magnetoresistance with increasing field. For alloys the drop is usually small compared with the residual resistivity; for example, Houghton, Sarachik, and Kouvel [137] report $\Delta\rho \sim 0.25 \mu\Omega \text{ cm}$ for a Cu 42at.% Ni specimen with a residual resistivity of $47 \mu\Omega \text{ cm}$. Pure ferromagnetic metals, on the other hand, may show very large changes. Takaki and Igaki [66] report a drop in ρ_0 from $\sim 40 \text{ n}\Omega \text{ cm}$ to $\sim 3 \text{ n}\Omega \text{ cm}$ for a polycrystalline iron specimen with $\text{RRR} = 2500$.

It is usually the resistivity at a given field and temperature that is important in applications. Figure 5.2 shows data for aluminum and copper. The message is clear: beyond a certain value it makes no sense to increase the purity, since the effect is compensated by the increased magnetoresistance.

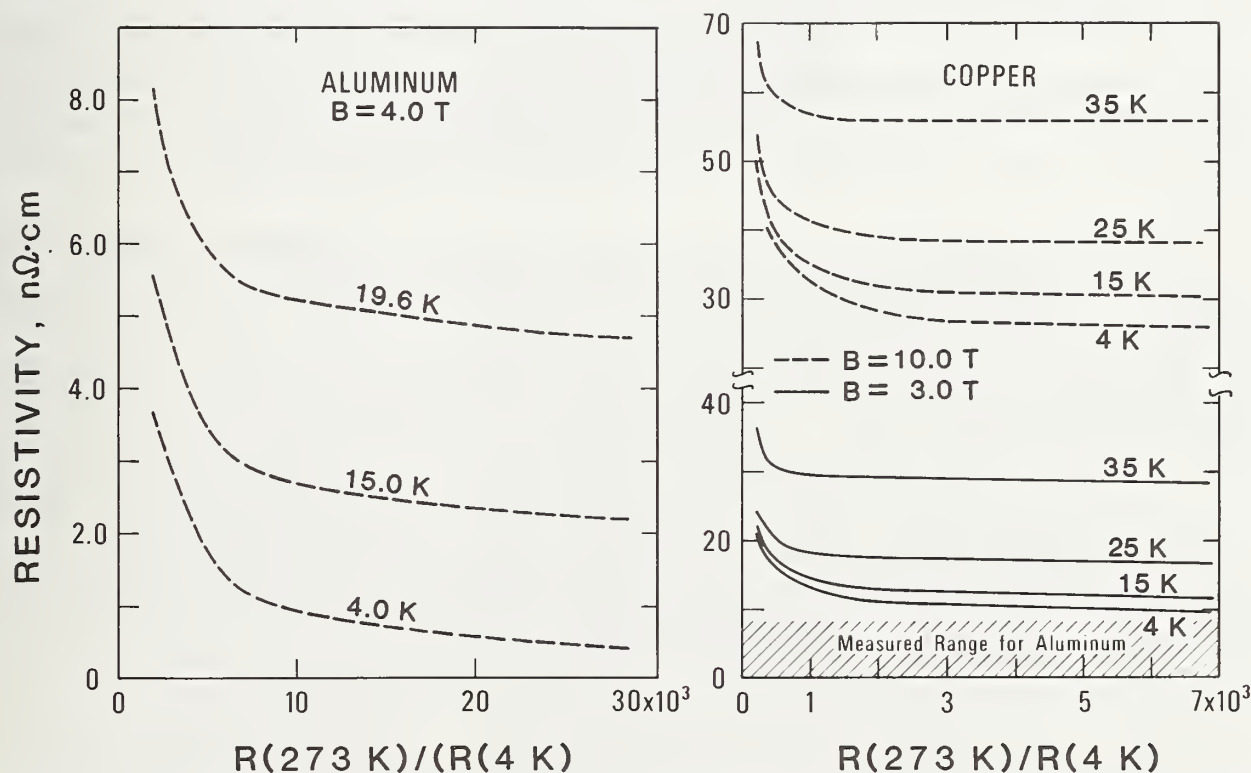


Figure 5.2. Resistivity as a function of purity as measured in the transverse configuration at several magnetic fields for aluminum and copper.

5.2 Hall effect

When a magnetic field is applied normal to a conductor carrying current, an electric field, E_H , appears across the conductor normal to both the magnetic field and the current. This field, the Hall field, is due to the Lorentz force on the current carriers. The Hall coefficient, R , is defined by the equation:

$$E_H = RJH \quad (5.2)$$

where H is the applied field and J the current density. This is a somewhat simplistic description, R actually is made up of off-diagonal elements of the tensor resistivity. The Hall field is an odd function of H . Sometimes voltages appear on the Hall field measuring probes that are even functions of the field (transverse even and planar Hall voltages). Thus, a measurement of R almost always requires reversal of both H and J .

The Hall voltages which arise in pure metals and alloys may be of either sign and tend to be very small. However, because R does not decrease greatly with decreasing temperature, the component of the Hall voltage that appears on misaligned voltage probes attached to a pure metal sample at 4 K can be very large compared with the resistive voltage. Typical data on the temperature dependence of R for simple metals are shown in figure 5.3, adapted from Alderson, Farrell, and Hurd [138].

In simple theory, R is proportional to the inverse of the number of conduction electrons. Its detailed behavior in various field regimes (R really isn't a constant at all) tells a great deal about the Fermi surface and the scattering interactions which occur on it. Furthermore, the Hall effect in semiconductors and semimetals (which have very low free electron concentrations) is very large (cf. $R \approx 5 \times 10^{-11} \text{ m}^3/\text{A s}$ for copper and $R \approx +10^4 \text{ m}^3/\text{A s}$ for indium-doped germanium) and usually increases with decreasing temperature. Thus, these materials are often employed in the measurement of magnetic fields.

There is an enormous amount of data available on the Hall effect for nearly any pure metal and for a surprising number of alloys. The comprehensive book by Hurd [139] covers the physics of the effect and reviews all of the data.

In magnetic metals an anomalous Hall effect occurs in which the Hall voltage rises linearly with applied field to a certain field value and then changes to a linear rise with a much lower slope. This behavior is seen not only in ferromagnetic metals, but also in other metals with strong localized moments. In fact, it may present a means of observing magnetic transitions in alloys, such as the paramagnetic to antiferromagnetic (or spin glass) transitions that occur at low temperatures in some stainless steels. Apparently no Hall effect data exist for the stainless steels.

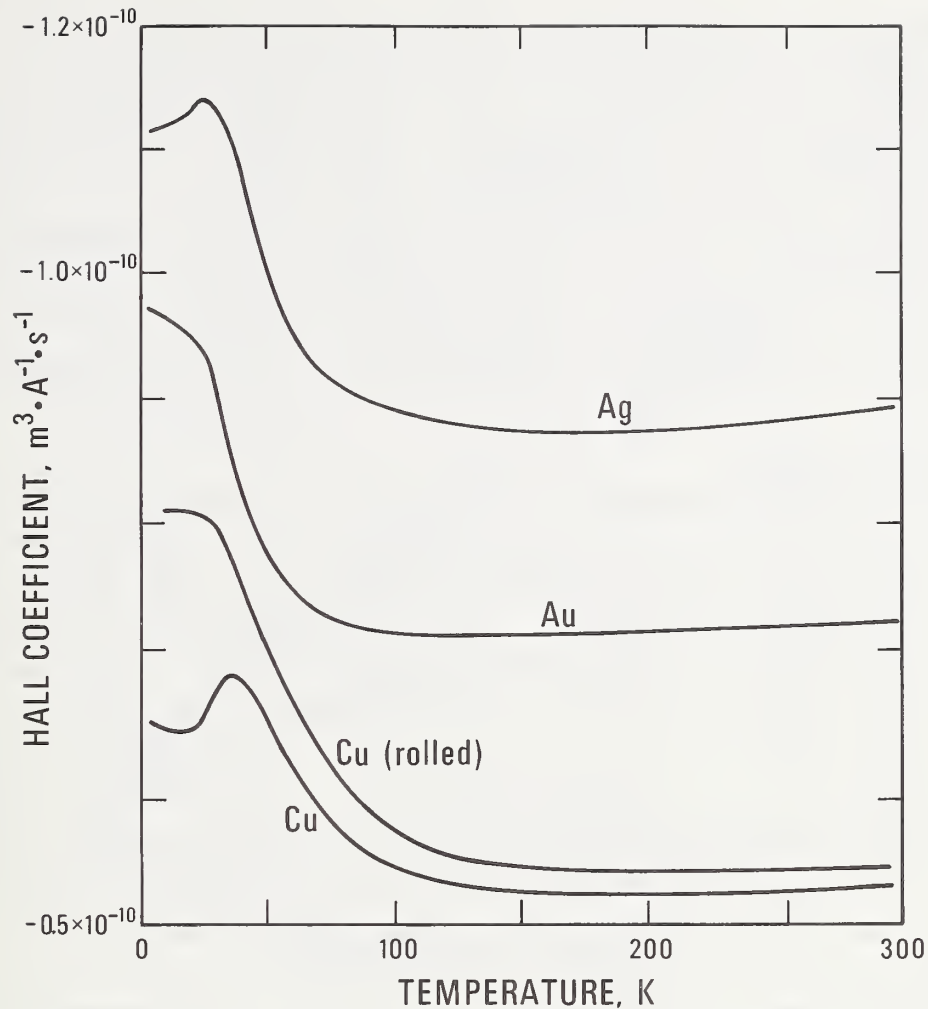


Figure 5.3. Temperature dependence of the Hall coefficient as measured by Alderson, Farrell, and Hurd [138] for very pure ("six nines") polycrystalline noble metals at 1.206 MA m^{-1} (15.16 kOe).

5.3 Pressure effects

It is not often that electrical conductors are subject to hydrostatic pressure in actual applications. Meaden [1] and Gerritsen [19] describe the experimental situation adequately. The early very comprehensive work of Bridgman on the resistivity variation of nearly all metals with pressure is still the standard. That work, and some later experimental results have been compiled and reviewed by Lawson [140]. Bundy and Strong [141] provide a further updating and a metal-by-metal review of the data.

Bridgman notes that there are 31 normal metals for which the resistivity decreases with increasing pressure. This group includes all of the commonly used metals. The changes induced in the room temperature resistance of most of these metals tend to be relatively small, varying from 1 to 5% of the resistivity at atmospheric pressure when measured at pressures to $\sim 10^8 \text{ kg m}^{-2}$. The percentage changes were observed to be somewhat larger at lower temperatures. At higher pressures ρ/ρ_0 becomes smaller. The total resistance decrease for copper at 10^9 kg m^{-2} was observed to be $\sim 13\%$ versus 1.9% at 10^8 kg m^{-2} .

The second group of metals, which includes the alkalis, semimetals and rare earths, shows a wide range of behavior, often with very large changes in resistivity. Nearly all the work that has been reported in the recent literature has been on these materials.

To return briefly to the case of copper, a particularly detailed experiment was performed by Dugdale and Gagan [142] on two commercial wire samples and one of copper containing 0.056 at.%Fe. They indicate that the rate of decrease of the intrinsic resistivity with pressure is temperature dependent and about four times higher at 4 K than at room temperature. On the other hand, the residual resistivity increases with pressure at temperatures up to 80 K, the rate of increase becoming smaller as the temperature increases.

5.4 Stress and fatigue

Application of either constant or variable stress to a conductor nearly always causes the resistivity to increase. At stress levels in the elastic range of the metal, the increase is reversible on removal of the stress. This effect is the basis of alloy strain gauges. As metals are stressed into the plastic region, irreversible changes occur as defects are formed. In real applications the defects described earlier never occur alone and seldom can the relative amounts of each be determined. The problem in conductor applications is to determine how the electrical resistivity changes as the metal is subject to the stresses and temperatures encountered in operation. The actual resistivity increase of a metal under stress is a strong function of many parameters including: (a) Temperature -- the lower the temperature, the greater the increase in resistivity for a given deformation; (b) Starting condition -- prior cold-work may increase the initial strain dependence of the resistivity; (c) Alloying elements -- in general a larger strain sensitivity is observed with increased alloying content. Some ordering alloys, however, may show a decrease in resistivity on straining; (d) Type of stress applied -- rolling, drawing, simple tension, shear, and compression all apparently give different results for the same amount of deformation, although the data are very limited.

One of the most important of these features from a low temperature application viewpoint is the effect of temperature of deformation on the resistivity, as illustrated in figure 5.4 for copper [143]. The tendency of the curves toward saturation is generally observed at large deformations. At a given low temperature the curves are fit by the empirical equation

$$\Delta\rho = K\epsilon^n \quad (5.3)$$

where K is a constant and $n \sim 1.0$ to 1.3 for aluminum [144] and 1.4 to 1.8 for copper [69]. Typical additional resistivities induced by strains of from 1 to 30% are in the range 1 to 200 $\mu\Omega$ cm in these two metals.

Metals which are severely deformed or irradiated at low temperatures show large increases in the residual resistivity. The resistivity of the annealed state is at least partially regained as the temperature is raised. The so-called recovery curve shows that

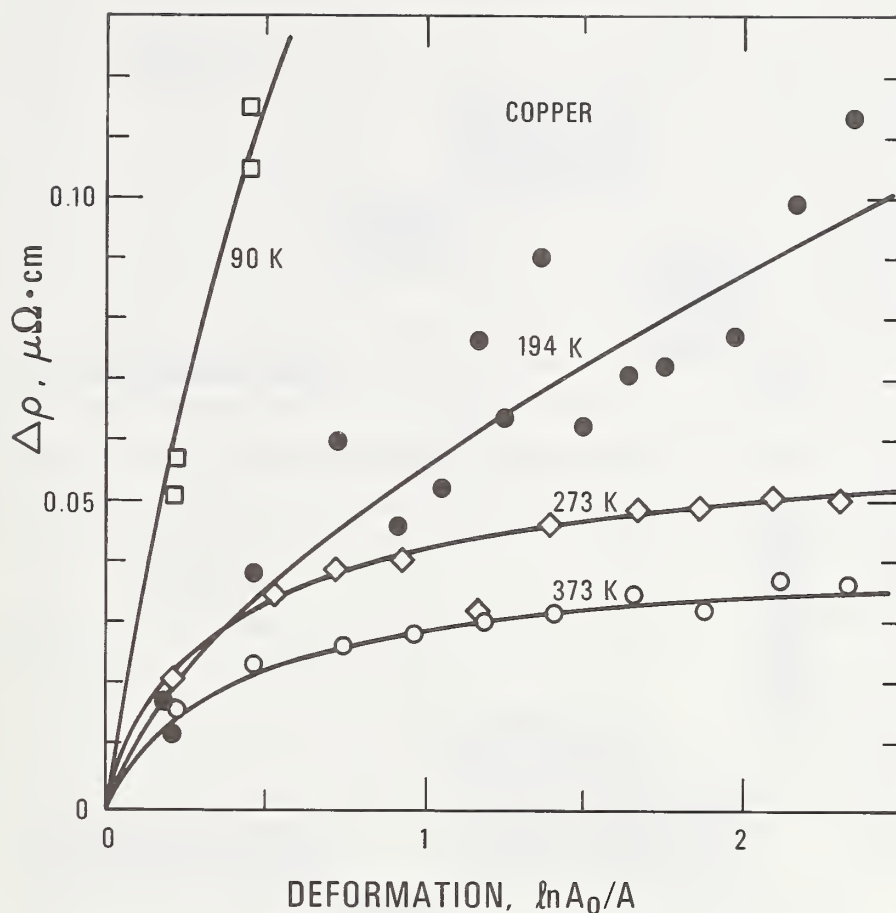


Figure 5.4. Effect of temperature on the resistivity increase due to deformation of copper by drawing [143].

the residual resistivity decreases in a number of stages which occur in rather well-defined temperature ranges. There are a total of five main stages, that may in turn show substage structure. The stages, in order of increasing temperature, are: I. Recombination of nearby vacancies and interstitials, most often seen in irradiated specimens. Many substages are observed. II. Recombination of diffusing vacancies and interstitials and migration to dislocations. III. Clustering of vacancies and migration of clusters. IV. and V. Annealing of dislocations in plastically deformed specimens. A schematic view of aluminum data compiled by Reed [145] is shown in figure 5.5. For a given material or test, some stages are not always well defined, and the mechanism operative in every case is not totally agreed upon. Often, one or more of the stages is not observed at all. The exact amount of recovery observed for each stage, and the range of temperature over which it occurs, depends on many factors, such as: (a) the specific metal and its chemical purity, (b) how the initial state of the metal came about, i.e., by irradiation, slight deformation, or large deformation, (c) the method of deformation or the type of particle used for irradiation.

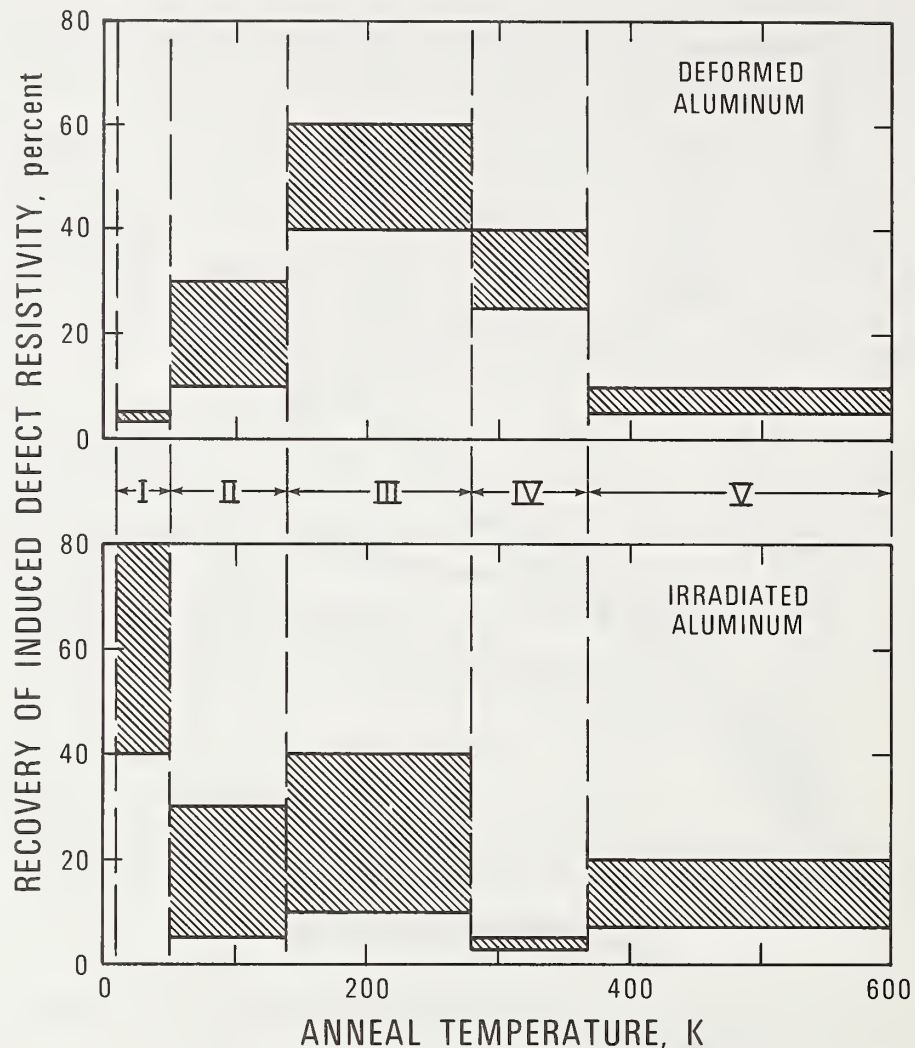


Figure 5.5. The recovery of aluminum as it is annealed through the five stages described in the text. The shaded ranges indicate the wide variations in recovery which may be observed at a given stage depending on the detailed parameters of the experiment.

Fatigue at low temperatures, even at relatively low strain values, can cause significant increases in the residual resistivity. The details, of course, depend on the amount of strain, the temperature, and the starting material. This is a topic of current interest, but not much is yet available in the way of data. The limited data which exist indicate that the resistivity rises rather rapidly in the first few cycles and then more slowly much like the curves of figure 5.4 if the abscissa were in cycles. Typical residual resistivities induced in pure copper by fatigue (0.2% constant strain) to several hundred cycles range from about $2 \eta\Omega \text{ cm}$ for $\text{RRR} = 2200$ starting material to $11 \eta\Omega \text{ cm}$ for $\text{RRR} = 223$ [146]. Recent measurements on copper as a function of strain (to 0.88%) and large numbers of cycles (to 10^5) show the resistivity increase to be exponential over the entire range [147].

Chapter 6. AC RESISTIVITY

The electrical resistivity of conductors can be significantly higher for alternating current than for direct current, even at quite low frequencies. This is especially true for the pure metals at low temperatures where the electronic mean free paths may be quite long. Furthermore, under ac excitation, power losses due to induced eddy currents occur even in the structural alloys. Although these losses are usually negligible at room temperature, the very low specific heat of all materials near 4 K can lead to unacceptable temperature excursions with very moderate power inputs by room temperature standards. In conductors the losses show up as undesirable increased impedances as well as producing the added heat loads. Ferromagnetic materials suffer additional complex losses because of their hysteretic behavior and temperature- and field-dependent permeabilities.

Dielectrics are most often associated with ac applications and, thus, a brief introduction to their low temperature electrical behavior is also included in this chapter.

6.1 The skin effect – classical and anomalous

Nearly all texts on electromagnetism (e.g., Jackson [148]) treat the case of the penetration of an electromagnetic wave into a conductor. The field energy is nearly entirely magnetic in nature and the wave is exponentially damped, decreasing to $1/e \approx 37\%$ of its surface value at a distance, δ , into the metal. δ is termed the classical skin depth, or penetration depth, and for good conductors, is given by:

$$\delta = (2\rho/\omega\mu)^{1/2} \quad (6.1)$$

where ω is the applied angular frequency and μ is the permeability in henrys per meter. Note that this equation is in MKS units and thus ρ must be expressed in ohm-meters and δ has the units of meters. The implication is that alternating currents may be concentrated quite near the surface of a conductor, and at very high frequencies (e.g., ~ 100 MHz where $\delta \approx 0.007$ mm for copper at room temperature) they may be described as "flowing entirely on the surface." On the other hand, at powerline frequencies the conductor size is usually less than a few skin depths and the current is not confined to the surface. Values of δ are shown in table 6.1 for metals with RRR = 1000 and a 1.0 Hz current, a rather modest and realistic set of values. Clearly, temperature has a dramatic effect on the ac behavior! Because the current distribution is changed, the inductance of the metal also will be lowered as the frequency increases. Calculation of the ac resistance, R_{ac} , of a given conductor configuration is a complex problem in differential equations. A variety of these calculations are presented by Stoll [149] and Lammeraner and Stafl [150]. The case of a circular wire of radius r is one of the easier to treat. The resulting equations are:

$$R_{ac}/R_{dc} = 1/4 + 4/2\delta + 3\delta/32r \quad \text{for } r \gg \delta \quad (6.2)$$

$$R_{ac}/R_{dc} = 1 + r^4/48\delta^4 \quad \text{for } r < \delta \quad (6.3)$$

These relationships are presented graphically in figure 6.1. To this scale, the highest order terms are negligible. This graph, in conjunction with table 6.1 shows that a wire that has essentially dc characteristics at room temperature ($r < \delta$) may exhibit a much higher resistance at 4 K where $r \gg \delta$.

Table 6.1. Skin depths for several metals at 1.0 Hz (RRR=1000)

Material	Temperature (K)	Skin Depth, δ (mm)
Copper	293	66
	4	2.1
Aluminum	293	82
	4	2.6
Iron ($\mu = 100$)	293	16
	4	0.5
Iron ($\mu = 1000$)	293	5.0
	4	0.16

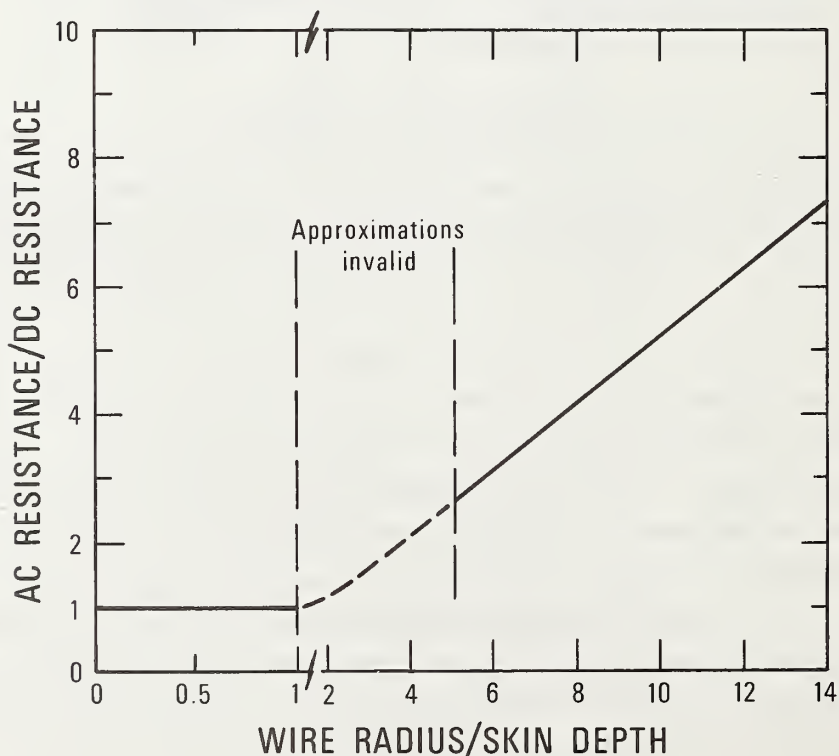


Figure 6.1. The effect of skin depth on the ac resistance of a circular wire.

Resistance increases can also occur due to the presence of other active or passive conductors. These can give a "reflected" resistance of significant size ($\sim 15\%$ of R_{ac}) at small separations. The details, again, depend strongly on geometry and the interested reader is referred to the texts just mentioned.

In the situations described above, the skin depth is assumed to be large compared with the electron mean free path. In nearly all practical situations this is justified, but at low temperatures it is not always the case and the anomalous skin effect must be considered. The theory is complex [151,82] but in essence it says that the only electrons which contribute to the conductivity are those travelling in such a direction that they do not leave the skin depth during the time required to travel one mean free path. Clearly, as the skin depth gets smaller, the directions satisfying this condition become fewer, approaching grazing incidence. The number of electrons available to carry the transport current become fewer, and the resistance increases. A detailed calculation, under a number of assumptions, shows the surface resistance then becomes independent of the purity of the metal and significantly larger than the value predicted by the classical skin effect. As an example, the anomalous skin effect becomes significant in pure aluminum ($RRR = 10000$) at 4 K for frequencies as low as ~ 10 Hz.

6.2 Eddy currents and magnetic diffusivity

The basic mechanisms responsible for eddy currents in conductors are just those alternating field effects described above. Nevertheless, eddy currents are normally considered as a separate dissipative mechanism caused by time-varying magnetic fields. With a few exceptions, such as their use in determining the resistivity of odd-shaped specimens (see section 2.3) and some shielding applications, they are quite undesirable in low temperature systems. They introduce unwanted heat into the system and they create magnetic fields that then interact with the inducing fields to give unexpected forces which can be quite large. Many of these problems become more severe at low temperatures. The effect of lowered specific heat has already been mentioned. The much lower resistivity of even commercially pure metals allows a changing field to induce currents that are orders of magnitude larger than would occur at room temperature. These, in turn, greatly increase the various reaction forces.

The easiest problem to analyze is a nonferromagnetic semi-infinite plate normal to the z axis with a sinusoidal field, H_x , parallel to its surface

$$H_x = H_s \cos \omega t \quad (6.4)$$

Maxwell's equations applied to this system lead to a diffusion equation:

$$\partial^2 H_x / \partial z^2 = (\mu / \delta) \partial H / \partial t \quad (6.5)$$

with the solution

$$H_x = H_s e^{z/\delta} \cos(\omega t + z/\delta) \quad (6.6)$$

where δ is the skin depth as defined above. Thus, the field decreases exponentially with increasing distance below the surface (the direction of $-z$), giving the classical skin depth. The peak field below the surface occurs $z/\omega\delta$ seconds after the surface peak, representing a diffusion of flux into the metal. The diffusion constant, or magnetic diffusivity, from eq (6.5) is therefore

$$D_{\text{mag}} = \rho/\mu \quad (6.7)$$

The magnetic diffusivity at 4 K tends to be on the order of $1 \text{ cm}^2/\text{s}$ for pure metals and several hundred cm^2/s for alloys. This number is frequently compared to the thermal diffusivity to determine whether eddy current heating can be removed by conduction as rapidly as it is generated, i.e., is $D_{\text{th}} > D_{\text{mag}}$? This aspect of eddy current heating is particularly important in superconducting magnet systems; it and other topics unique to those systems are treated by Brechna [152].

The calculation of the power dissipated by eddy currents is strongly related to the geometry of the structure and most often requires complex mathematical techniques for a general solution. Stoll [149] gives many useful techniques and examples. For a flat plate with two sides (reasonably conventional) and of thickness a , located in a parallel uniform field, the losses per unit area, P_{ec} , in the limiting cases are given by

$$P_{\text{ec}} \approx H_s^2 \rho/\delta, \quad a \gg \delta \quad (6.8)$$

and

$$P_{\text{ec}} \approx H_s^2 (\rho/\delta) (a^3/6\delta^3), \quad a \ll \delta \quad (6.9)$$

The SI units of power loss are watts per square meter. It is important that the proper equation be used. The frequency dependence of the losses is quite different in the two cases, varying as $\omega^{1/2}$ in eq (6.8) and as ω^2 in eq (6.9). In the first case, the eddy currents are said to be inductance limited, and in the second, resistance limited. As long as the simple inequalities $a > \delta$ and $a < \delta$ are not violated, results accurate to $\sim 10\%$ can be obtained from the above formulas.

Since the skin depth drops as $\rho^{1/2}$ as the temperature is lowered, it is quite possible that a switch from one inequality to the other may occur somewhere along the line for pure metals. An aluminum plate 1 cm thick with RRR = 10000 and in a 1 Hz field has $\delta = 82 \text{ mm}$ at room temperature and $\delta = 0.82 \text{ mm}$ at 4 K. If the peak field is 3 tesla ($H = 2.4 \text{ MA/m}$), the losses at room temperature will be 560 W/m^2 by eq (6.9) and 1866 W/m^2

by eq (6.8) at 4 K! By the way, if one had persisted (wrongly) in using eq (6.9) at 4 K the result would have been more than seven orders of magnitude larger!

In the calculations outlined here, the possibly large effect of magnetoresistance in some very pure metals, notably copper, has been neglected. The increased resistance in very high fields will always result in decreased eddy current losses, but exact calculations require detailed information on the specific material.

In the construction of high-power transmission lines the conductor is a cable made up of smaller wires, both to minimize eddy current losses and to insure that a nearly uniform current distribution exists throughout each separate wire (i.e., negligible skin effect) so as to make optimum use of the metal. Further, to insure that each wire carries the same current the separate wires are transposed.

The ac losses that occur in ferromagnetic materials are even more complex. The various analyses outlined above for eddy current effects usually hold, but the permeability, μ , is no longer independent of H , and this fact introduces nearly insurmountable problems for the various loss calculations. The only new low temperature complication comes about because the value of μ is also temperature dependent. For some metals the resistivity may be a strong and complex function of field, which complicates the calculations, but this is only likely in the case of pure ferromagnetic metals. The result of these effects is that the skin depth and magnetic diffusivity may become strongly dependent on the instantaneous value of the applied magnetic field.

Hysteresis losses often exceed the eddy current losses in magnetic steels and other losses occur under ac excitation related to such phenomena as domain wall motion. For the most part, these effects are not strongly temperature dependent and their description is best left to the many excellent treatments of room temperature behavior, such as the book by Heck [153]. The temperature dependent phenomena will be treated in a later monograph [154].

6.3 Dielectrics

Polymers and other solid dielectric materials are extensively employed at low temperatures as electrical insulators, thermal insulators, and in the case of fiber reinforced materials, as structural members. In their electrical insulator role it is most often the ac properties which are of concern, although there are also problems in dc applications. Most of the relatively small amount of available information on the ac electrical properties of dielectrics at low temperatures has been accumulated over the last decade as a result of the interest in cryogenic or superconducting powerlines. Detailed discussions of the materials problems associated with superconducting powerlines are given in the book by Rechowicz [155] and the review by Bogner [156].

Application of laboratory data on pure dielectric materials to the design of actual structures is difficult because of a host of geometrical and environmental effects, which often prove to be more severely limiting than the bulk properties. Another difficulty is that these materials are seldom well characterized or uniform in composition. The degree of crystallinity of polymers and the porosity of commercial fiberglass epoxy materials are

two examples of properties that may vary over wide ranges and that can have significant effects on the low temperature electrical properties. Existing electrical properties data are reviewed in the texts just mentioned and in more detail by Fallou [157]. A compilation of low temperature electrical and mechanical properties data for six polymers is also available [158]. A recent paper [159] describes the 4 K electrical properties at giga-Hertz frequencies for a number of materials. A few other papers on specific polymers are listed by Johnson [160].

The properties of dielectrics are strongly influenced by the degree of charge separation created by an applied electric field. Polar dielectrics show a large effect, while little change is observed for the nonpolar materials. The polar or nonpolar nature of a particular material is best determined from the literature on that material. Some examples of nonpolar dielectrics are polyethylene, polypropylene, and polytetrafluoroethylene (TFE); polar dielectrics are paper, polyethylene terephthalate (PET) and poly-pyromellitimide (PPMI).

The properties of interest in electrical applications are:

- a. Breakdown Strength (dc, ac, and impulse);
- b. Dielectric Constant (ϵ); and
- c. Loss Tangent ($\tan \delta$).

The breakdown strengths for polymers tend to be tens of kilovolts per mm of thickness and are not greatly affected by temperature. Some polar dielectrics show increases as large as 10 to 20% on cooling to 4 K. Knowledge of this property is almost always of no value except as a means of material comparison. In real situations, the breakdown usually occurs at much lower electric fields due to surface flashover or interactions between the dielectric and the cryogen or gas in which it is located. Many specific cases are discussed in the references given above. Another property, the volume resistivity, is sometimes measured. This parameter gives an indication of the number of available free carriers, and is usually measured in conjunction with radiation damage studies.

The dielectric constant determines the capacitance of a system. Generally, small values are desirable since high capacitances result both in high charging currents and in high ac losses. It is hard to generalize, but some comments can be made. Most often the dielectric constant of nonpolar dielectrics is not greatly temperature dependent. That of the polar dielectrics tends to decrease with decreasing temperature. The dielectric constant is significantly higher, often by more than an order of magnitude, for polar materials than for nonpolar ones, even at low temperatures. Some typical temperature dependences measured at low frequency are shown in figure 6.2. Frequency has little effect on the shape of the temperature dependence curve, although an overall decrease (<10%) in magnitude is often seen for the polar materials with increasing frequency to the low giga-Hertz range.

The loss tangent expresses the sum of a number of loss mechanisms which occur because dielectric materials are not perfect and molecules and free charges exist which can be moved around in various ways by the applied electric field creating heat at the expense of electrical energy. In the case of ac power transmission the power loss is given by

$$P = \omega C V^2 \tan \delta \quad (6.10)$$

where $1/\omega C$ is the capacitive reactance and V is the applied ac voltage. Typical values of $\tan \delta$ for polar materials at 4 K are 10^{-3} to 10^{-4} , whereas the nonpolar materials have values below 10^{-5} . Some typical curves as a function of temperature are shown in figure 6.2. Many peaks and valleys occur, but the loss tangent generally decreases with decreasing temperature and most of the erratic behavior is over at 4 K. This is consistent with a picture in which many of the dissipative molecular motions are "frozen" at low temperatures. The effect of frequency on the loss tangent is widely variable and no generalizations can be made.

When all of the uncertainties are combined with the large thermal contraction and rapid embrittlement of most of these materials, their use at low temperatures becomes an exercise in frustration, and it is clear that no totally acceptable dielectric material exists at present. Future directions appear to be toward chemically tailoring some of the more promising polymers, evaluating mixtures of polymers and polymers filled with low-loss powders, and evaluating a few promising nonpolymeric materials.

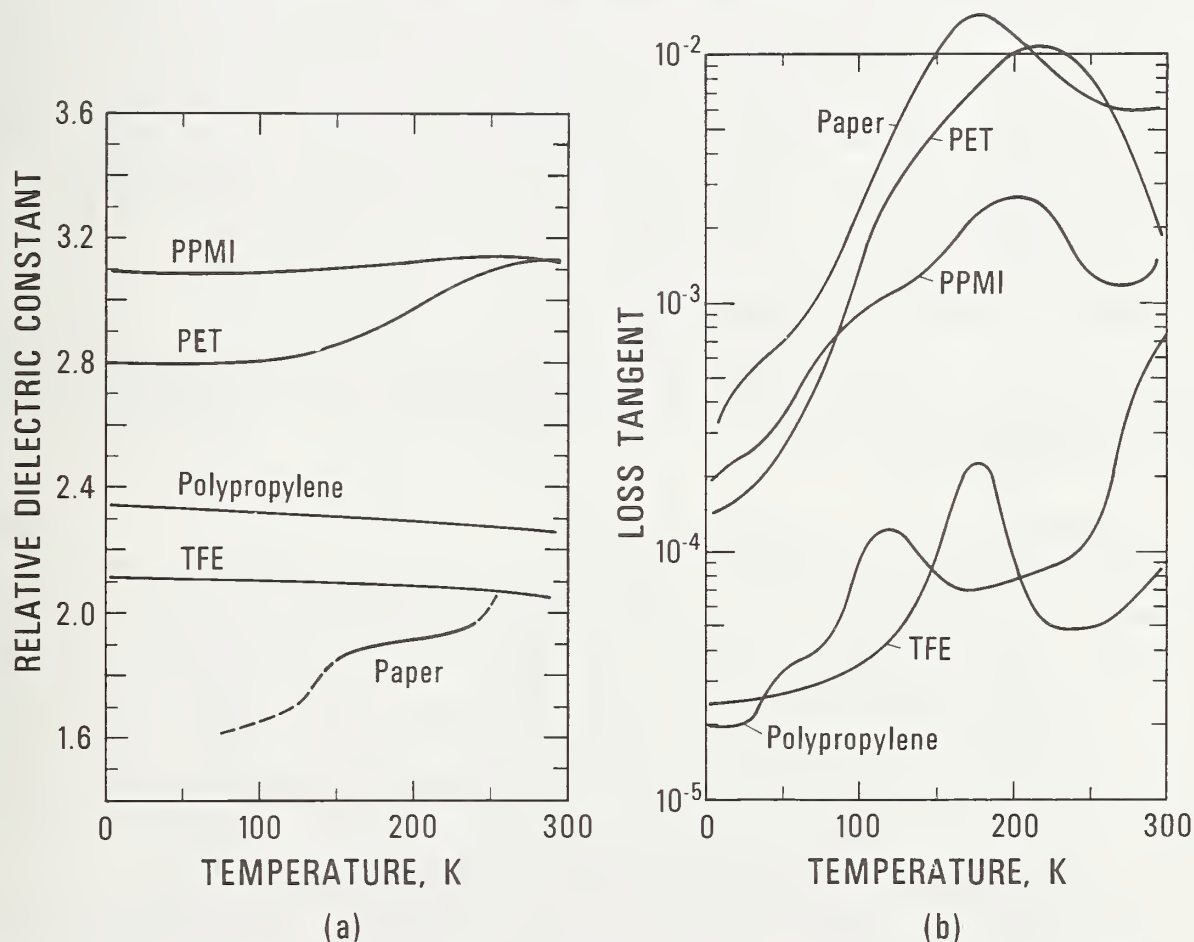


Figure 6.2. The effect of temperature on the relative dielectric constant (a) and the loss tangent (b) of several common dielectrics at near powerline frequencies. All data except those on the paper dielectric are from Chang [161] and were measured at 75 Hz. The data on paper are from Allen and Kuffel [162] as measured at 47 Hz.

Chapter 7. LOW TEMPERATURE ELECTRICAL PROPERTIES OF SPECIFIC METALS AND ALLOYS

The aim of this chapter is to provide information which will help the reader to find and interpret the existing resistivity data on metals and alloys and to use those data in conjunction with his own measurements to determine resistance behavior over a wide temperature range. The metals considered are primarily those with technological applications at low temperatures.

Few sources of compiled data on the electrical resistivity as a function of temperature exist. The documents by Stewart and Johnson [163] and Hall [5,7] and the tabulation by Meaden [1] cover a number of pure metals. Copper is treated in detail by Welles [69] and aluminum by Milek and Welles [164]. Data on both pure metals and structural alloys are compiled in the Handbook on Materials for Superconducting Machinery [165]. A large amount of the alloy data is from Clark et al. [15]. Other sources of alloy resistivity data at low temperatures are two handbooks dealing primarily with mechanical properties: the Materials Properties Data Book [166] and the Aerospace Structural Metals Handbook [167].

Often the handbooks present curves of resistivity as a function of temperature without showing the actual data points. For a few metals so much data exists that this is the only practical approach, but usually the situation is quite the opposite. Thus, this practice frequently masks the fact that the measurements were made at only three or four temperatures and a solid curve on the graph does not guarantee that the resistivity is actually known over the entire range. This is especially a problem in the range 10 to 77 K where many metals are showing the first significant deviations of the resistivity from residual behavior with increasing temperature.

Room temperature resistivity data on 31 commercial alloys is given in the Handbook of Chemistry and Physics [168] and data on 129 noncommercial alloys is presented in the Metals Reference Book [55].

7.1 Conductors

All of the metals which have been seriously proposed for conductor applications below room temperature have been at least of commercial purity ($RRR \gtrsim 50$) or better. Because of the effects of handling and the problems of manufacture, it seems unlikely that materials with $RRR > 10,000$ will ever find very wide use. The metals of most interest are polycrystalline copper, aluminum, nickel, and beryllium. Sodium has been used for power transmission applications at room temperature, but its use has been discontinued because of a variety of problems. It has been discussed as a low temperature conductor, but the problems become even more formidable at cryogenic temperature [156].

Figures 7.1 and 7.2 show plots of the intrinsic resistivity for copper and aluminum as determined by the Bloch-Gruneisen formula (eq 3.1) and the measured room temperature resistivity. A very good estimate of the resistivity of a given material at any temperature can be obtained by measuring the residual resistivity and adding that value to those given in the figures. The Bloch-Gruneisen formula does not describe the very low temperature resistivity for very pure metals with great accuracy, but it represents the most

reasonable approach and will result in usable data, at least for purposes of estimation. If better data are needed, the only option is to actually make the measurement.

The figures also show actual data points from one measurement to indicate how the technique outline above may be applied. The serious user will need to make a larger graph; table 7.1 provides the data. Calculated values for nickel and beryllium are also included in the table.

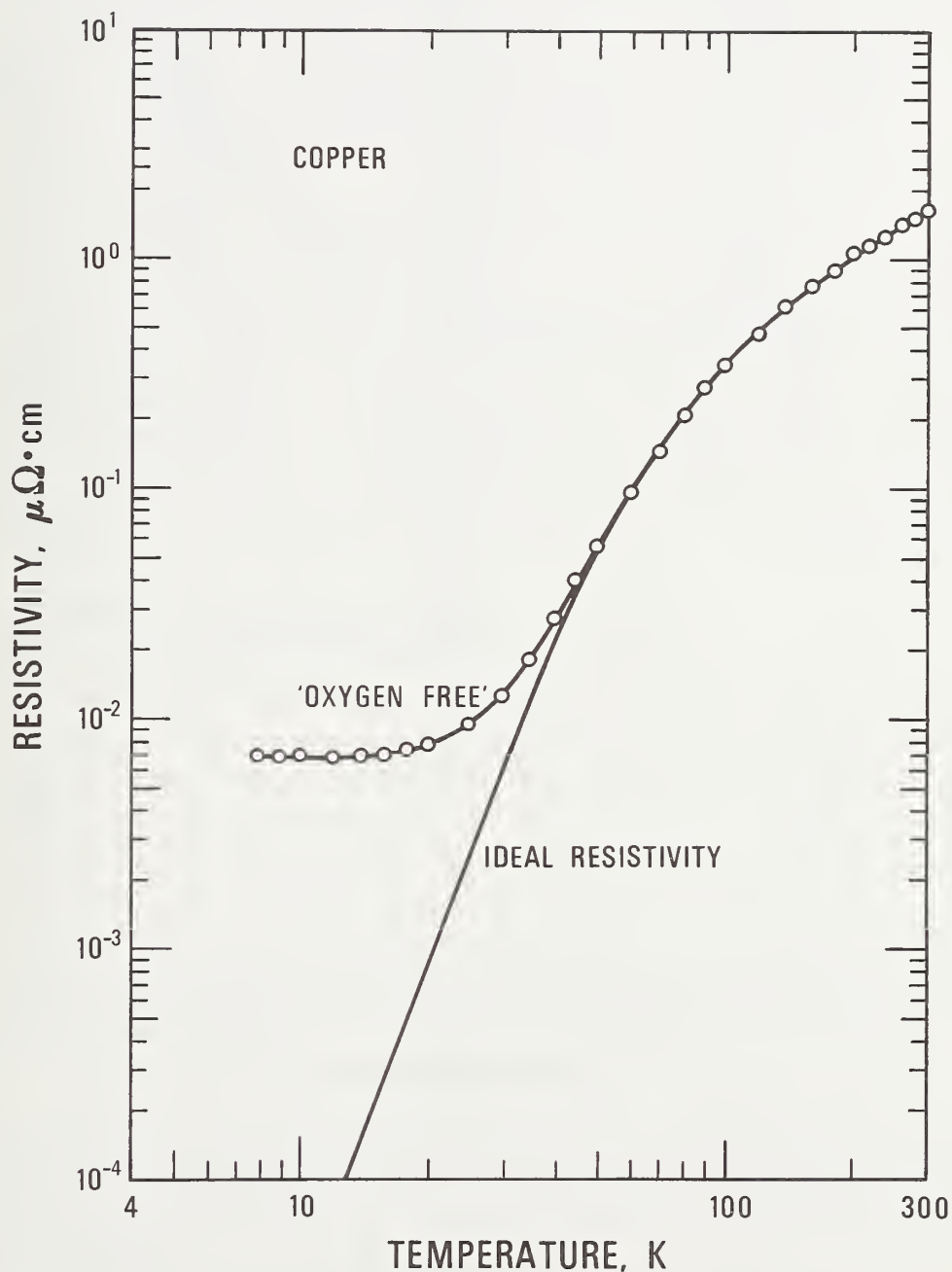


Fig. 7.1 The intrinsic resistivity of copper calculated from the Bloch-Gruneisen formula using $\Theta = 330$ K and $\rho(273 \text{ K}) = 1.553 \mu\Omega \cdot \text{cm}$. Data for "oxygen free" copper as measured by Hust and Giarratano [169] are shown also.

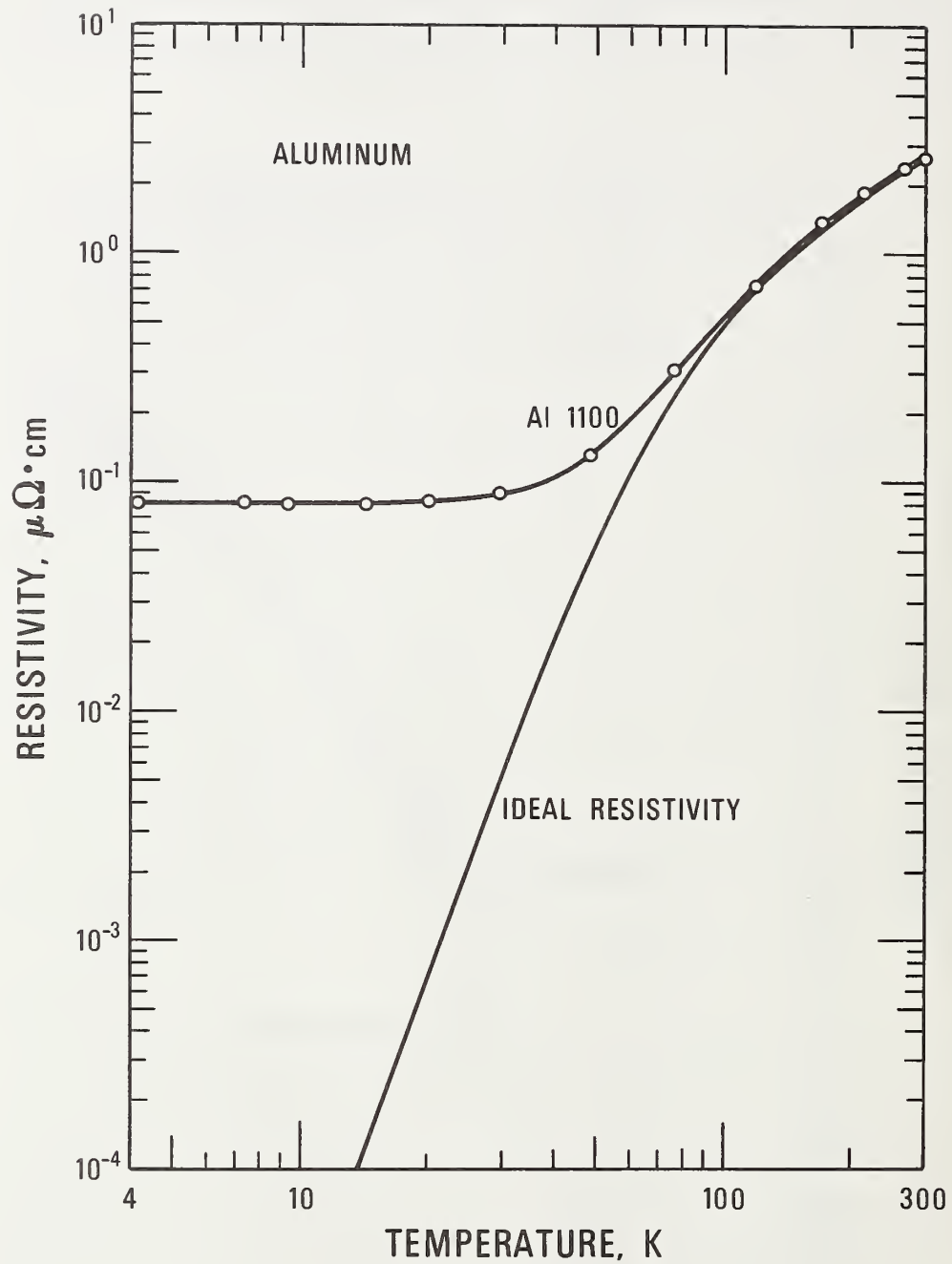


Fig. 7.2 The intrinsic resistivity of aluminum calculated from the Bloch-Gruneisen formula using $\Theta = 400$ K and $\rho(273 \text{ K}) = 2.428 \mu\Omega \text{ cm}$. Data for the 1100 alloy as measured by Clark and Sparks [170] are shown also.

Table 7.1. Intrinsic resistivity values for several metals

Temperature (K)	Resistivity ($\mu\Omega$ cm)			
	Copper $\theta = 330$ K	Aluminum $\theta = 400$ K	Nickel $\theta = 400$ K	Beryllium $\theta = 1300$ K
300	1.728	2.720	6.976	3.460
295	1.696	2.666	6.837	3.313
273	1.553	2.428	6.229	2.70
250	1.400	2.174	5.581	2.095
225	1.232	1.896	4.867	1.510
195 (CO ₂)	1.028	1.556	3.995	0.9203
175	0.8901	1.326	3.407	0.6100
150	0.7142	1.035	2.656	0.3226
125	0.5353	0.7432	1.903	0.1417
100	0.3556	0.4604	1.182	4.846×10^{-2}
90	0.2852	0.3549	0.9109	2.882×10^{-2}
77.3 (LN ₂)	0.1997	0.2325	0.5969	1.349×10^{-2}
70	0.1541	0.1712	0.4393	8.289×10^{-3}
60	9.819×10^{-2}	0.1007	0.2586	4.687×10^{-3}
50	5.307×10^{-2}	4.951×10^{-2}	0.1271	1.530×10^{-3}
40	2.213×10^{-2}	1.861×10^{-2}	4.776×10^{-2}	5.047×10^{-4}
27.2 (LNe)	3.782×10^{-3}	2.889×10^{-3}	7.416×10^{-3}	7.312×10^{-5}
20.4 (LH ₂)	9.114×10^{-4}	6.904×10^{-4}	1.773×10^{-3}	1.734×10^{-5}
10	2.608×10^{-5}	1.942×10^{-5}	4.987×10^{-5}	4.893×10^{-7}
4.2 (LHe)	3.402×10^{-7}	2.538×10^{-7}	6.516×10^{-7}	6.399×10^{-9}

7.2 Structural alloys

The data on these alloys are quite limited, particularly if accurate values are required at closely spaced temperatures. Fortunately, from the data that do exist, it appears that most of these alloys show regular behavior with decreasing temperature. In nearly all cases, the resistivity decreases quite linearly to about liquid nitrogen temperature and then tends to flatten out to a residual value, usually around 20 K. In some nickel alloys a slight minimum is observed, usually above 20 K. In general, the more highly alloyed metals show a higher resistivity at all temperatures, but the curves often tend to be quite parallel for all members of an alloy series, as shown in figure 7.3 for aluminum alloys. For most alloys the residual resistivity ratio is two or less and is, thus, not a very meaningful quantity. Table 7.2 from Clark et al. [15], lists resistivity values for a large number of alloys that have been used at low temperatures. This table is the source of most of the alloy data found in modern compilations. This information is particularly valuable in estimating the eddy current heating in large structures.

7.3 Other materials

There are, obviously, many metallic elements and alloys that have not been mentioned here. The complete task would take several volumes and each material would be of very limited interest. A search of the files of the National Bureau of Standards Cryogenic Data Center yielded approximately 1400 references on resistivity alone. It seems that the

resistivity of nearly every alloy imaginable has been measured at some low temperature or other. For information on a specific material, a search of the many computer systems now available is suggested. The Cryogenic Data Center at NBS has now been closed. The Metals and Ceramics Information Center (MCIC) at the Battelle Columbus Laboratories, Columbus, Ohio is an excellent source of bibliographies. A relatively recent MCIC publication [160] on low temperature materials properties gives an up-to-date bibliography that covers electrical properties of many of the materials discussed here, including some nonmetallics.

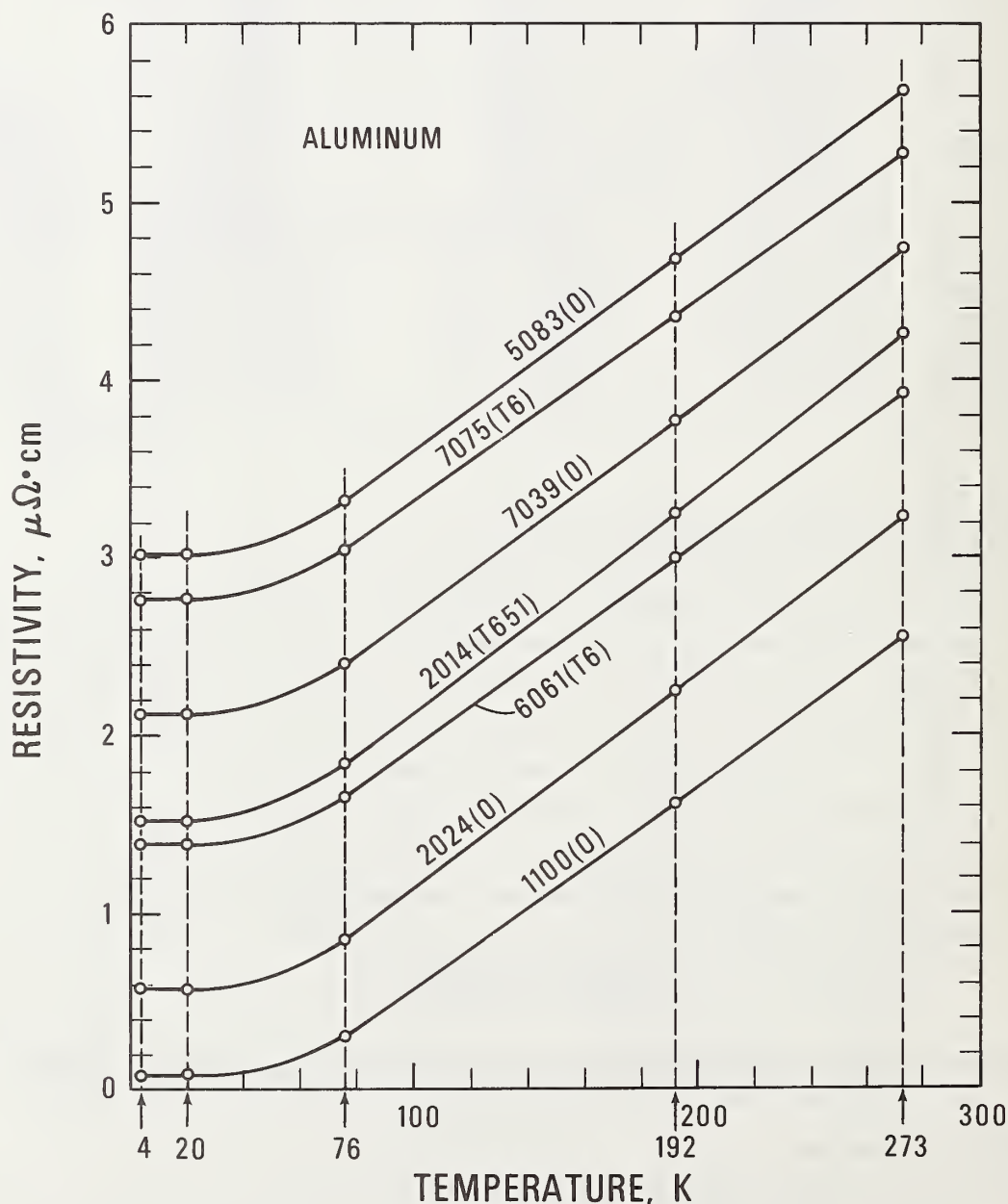


Fig. 7.3 The electrical resistivity of a number of aluminum alloys as measured by Clark et al., [15].

Table 7.2. Electrical Resistivity of Alloys at Low Temperatures. From [15].

Material ^a	Electrical Resistivity, $\mu\Omega$ cm				
	273 K	192.4 K	75.75 K	19.65 K	4.0 K
Al 1100 (O)	2.67	1.617	0.310	0.084	0.082
Al 2024 (T651)	4.27	3.26	1.839	1.535	1.531
Al 2024 (O)	3.24	2.25	0.854	0.586	0.583
Al 2024 (T4)	4.35	3.39	2.02	1.745	1.742
Al 2024 (T6)	4.00	3.02	1.624	1.341	1.337
Al 2024 (T86)	4.21	3.23	1.866	1.581	1.578
Al 5083 (H113) (across)	5.71	4.74	3.36	3.07	3.07
Al 5083 (H113) (with)	5.68	4.72	3.34	3.05	3.05
Al 5083 (O)	5.66	4.69	3.32	3.03	3.03
Al 6061 (T6)	3.94	3.00	1.656	1.385	1.381
Al 7039 (T61)	4.37	3.40	2.02	1.741	1.738
Al 7039 (O)	4.75	3.78	2.40	2.12	2.12
Al 7075 (T73)	3.77	2.77	1.375	1.095	1.092
Al 7075 (T6)	5.29	4.36	3.04	2.77	2.76
Hastelloy C	126.8	125.8	124.0	123.1	123.3
Hastelloy N	120.6	120.0	119.5	119.4	120.1
Hastelloy X (annealed)	113.8	111.6	108.3	107.2	107.6
Hastelloy X (brazed)	115.0	112.9	109.4	108.1	108.7
Inconel 625	127.7	126.6	124.8	123.9	123.4
Inconel 718 (a)	114.5	112.1	108.3	107.7	108.1
Inconel 718 (b) (aged)	106.6	103.6	99.2	98.4	98.8
Inconel 718 (b) (annealed)	122.5	121.4	118.5	118.3	118.8
Inconel X (aged)	122.9	121.0	118.3	117.3	117.6
Inconel X (annealed)	124.5	123.1	121.0	120.4	120.9
Rene 41	126.3	123.9	120.0	118.3	118.1
TD Nickel	6.73	3.87	0.741	0.185	0.173
Udimet 630	112.2	109.4	105.1	104.1	104.5
Udimet 700	131.5	127.5	120.7	117.4	116.5
Waspaloy (aged)	119.1	116.0	110.8	108.7	108.2
Waspaloy (annealed)	124.3	121.9	117.9	116.0	115.4
OFHC Cu	1.559	1.013	0.200	0.017	0.016
OFHC Cu (60% CD)	1.581	1.034	0.222	0.032	0.031
Amzirc	1.730	1.177	0.364	0.163	0.163
Berylco 25 (annealed)	10.51	9.68	8.49	8.18	8.21
Berylco 25 (precipitation-hardened)	9.21	8.40	7.24	6.92	6.92
Aluminum Bronze D	16.2	15.3	14.0	13.8	13.9
Ni-Al Bronze	18.35	17.39	15.97	15.66	15.74
Phosphor Bronze A	10.48	9.83	8.88	8.58	8.59
Cartridge Brass, 70%	6.65	5.85	4.65	4.22	4.22
Commercial Bronze, 90%	3.90	3.29	2.38	2.10	2.11
Admiralty Arsenical	6.93	6.15	4.97	4.56	4.56
Naval Brass	6.32	5.41	3.89	3.28	3.25
Red Brass, 85%	4.66	4.00	3.02	2.72	2.74
CuNi 10	18.39	17.75	16.86	16.72	16.65
CuNi 30	38.4	37.8	36.7	36.5	36.4
CuNiSi (aged)	3.87	3.30	2.45	2.21	2.21
CuNiSi (annealed)	7.11	6.53	5.66	5.41	5.43
CuSi-A	23.2	22.5	21.5	21.4	21.3
Ti-5Al-2.5Sn	160.4	152.2	139.0	135.4	135.7
Ti-6Al-4V	167.5	161.0	150.1	146.9	--
Ti-6Al-4V (ELI)	156.3	149.0	136.6	133.1	--
Ti-13V-11Cr-3Al	149.2	150.9	155.1	157.4	156.7
AISI 670 (Co Haynes 25)	94.6	91.7	87.0	84.8	83.9
AISI 302	71.0	63.6	51.9	49.5	49.6
AISI 303	70.7	63.1	51.1	49.1	49.3
AISI 304L	70.4	63.0	51.4	49.4	49.6
AISI 310	87.3	81.7	72.4	68.8	68.5
AISI 316 (b) (cold drawn, annealed)	76.5	69.7	58.5	55.3	55.3
AISI 316 (c) (cold drawn, annealed)	77.6	70.7	59.5	56.3	56.3
AISI 316 (d) (annealed)	75.0	67.9	56.6	53.8	53.9
AISI 316 (e) (cold drawn, annealed)	71.8	64.3	52.3	50.2	50.3
AISI 321	73.9	66.8	55.6	53.4	53.6
AISI 347	70.8	63.4	51.9	50.0	50.1
AISI 410	55.9	48.7	39.5	38.2	38.2
AISI 416	66.2	60.4	53.4	52.3	52.3
AISI 430F	58.9	51.0	40.9	39.4	39.4
AISI 440C (hardened)	61.0	55.6	49.0	47.9	47.8
AISI 440C (annealed)	61.0	55.7	49.1	47.9	47.8
AISI 4340	31.0	25.8	19.27	18.16	18.15
AISI 630 (17-4 PH)	101.7	99.7	97.1	96.8	96.9
AISI 631 (17-7 PH) (annealed)	101.5	99.5	96.9	96.7	96.8
AISI 631 (17-7 PH) (precipitation-hardened)	70.9	65.8	57.8	57.6	57.5
AISI 632 (PH 15-7 Mo)	80.0	73.5	63.2	61.5	61.6
PH 13-8 Mo	100.1	98.1	95.3	94.9	95.0
AISI 633 (annealed)	64.4	57.7	44.2	43.2	43.3
AISI 633 (precipitation-hardened)	74.5	68.9	60.7	59.5	59.5
Fe-29 Ni	35.4	28.4	22.4	21.1	20.9
Invar 36	79.5	69.0	54.4	50.5	50.2
LR 35	71.9	59.5	43.8	40.2	40.0
Fe-50 Ni	39.2	29.2	19.5	17.6	17.4
Fe-79 Ni	20.6	16.3	12.2	11.5	11.4

^aThe use of tradenames is for material identification only and in no way implies endorsement by NBS.

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